### STUDIES ON MIXED COMPLEXES

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

by
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to the

DEPARTMENT OF CHEMISTRY

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### STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India under the supervision of Professor A. Chakravorty.

In keeping with the general practice of reporting scientific observations, due acknowledgement has
been made whenever the work described is based on the
findings of other investigators.

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Kanpur: July 1977

### CERTIFICATE I

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B.S. Raghavendra

#### PREFACE

Much of the chemistry described in this thesis can be broadly divided under two headings: (i) mixed-ligand type and (ii) mixed-metal type. Our original interest in mixed complexes centred around mixed ligand complexes of composition M(Lb)(Lt), where Lb and Lt are potentially bidentate and tridentate ligands. Old results are summarised in Chapter I and new results are presented in Chapters II and III. Examples of the type  $M(ligand)_n X_n$ , where X is a halogen atom can be found in Chapter IV. In Chapters IV and V the ligand systems used contain the azoimine fragment. The mixed metal complexes of Chapter V include the combination Fe(II), Na(I); Fe(II), Fe(III). The latter comes under the mixed valence category. molecular systems are described in this thesis. The major emphasis is on structure elucidation using a number of spectroscopic, magnetic and other techniques. Admittedly the final answer to a structural problem lies in most cases in diffraction work. Yet there is joy in trying to grope in dimmer light of indirect techniques, the shape of these molecules. We have enjoyed doing the little that has been reported in the pages to follow. Our efforts will remain fully rewarded if the reader finds at least a few enjoyable items. Inspite of all attempts, unintentional oversights and errors will be present in the thesis. author is responsible for all this.

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#### CHAPTER I

SOME ASPECTS OF THE M(bidentate) (tridentate) SYSTEM

Abstract: The stereochemical pattern in various mixed-ligand systems of the type M(bidentate) (tridentate) are reviewed in this chapter. Examples are cited where the metal atom is pentacoordinated. In other cases octahedral geometry results from dimerisation or adduct formation. In a number of cases stereochemical equilibria are identifiable in the solution phase.

### I.1 INTRODUCTION

The work described in the next two chapters originated as part of our studies on the design of mixed-ligand molecules of the type M(bidentate) (tridentate). Some synthetic and structural aspects pertaining to this system are summarised in this chapter.

### I.2 GENERAL CONSIDERATION

A monomeric complex of the formula M(Lb)(Lt) (where Lb = bidentate ligand and Lt = tridentate ligand) in which all the potential coordinating atoms are bonded to metal will be pentacoordinated. This is a very simple strategy which however, has been rarely used in practice. Examples will be given in the next section.

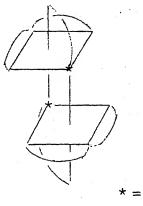
The occurrence of pentacoordination in M(Lb)(Lt) systems may be hindered by various factors some of which are noted below:

### (i) Facile disproportionation reaction

$$2M(Lb)(Lt) \longrightarrow M(Lb)_2 + M(Lt)_2$$
 (1)

in which the products need not have pentacoordinated geometry.

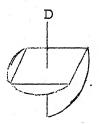
(ii) <u>Dimerisation</u> Leading to  $M_2(Lb)_2(Lt)_2$  in which the metal atom may be pseudooctahedral as shown below (I):



\* = bridging atom

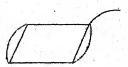
(I)

(iii) Adduct formation with Lewis base (D) giving pseudooctahedral geometry (II):



(II)

(iv) Lack of complete coordination for example, the Lt unit can actually act as a bidentate ligand giving rise to four-coordinated complexes (III):



### I.3 SOME RESULTS

The best known early example belonging to the M(Lb) (Lt) class is probably M(diars) (triars)  $^{2+}$  which is low-spin and has the sp coordination sphere as shown in (IV):

The synthesis and identification of this complex has an interesting history. 1-3 It was first obtained under conditions when no one expected it. Eventually however, it was prepared by reacting nickel(II) perchlorate with a mixture of diars and triars. Recently a similar complex having the NiAs<sub>4</sub>Sb coordination sphere is reported. 4

Certain bis complexes of the Schiff bases of the type (V) have been shown to have pentacoordinated geometry:

Examples are: M(5-Cl-salenNEt<sub>2</sub>)<sub>2</sub><sup>5,6</sup> (M=Ni(II), Co(II)) and Cu(salenNMe<sub>2</sub>)<sub>2</sub>. The these cases the ligands are potentially tridentate. However, in the bis complexes one of the two ligands uses only two of the three coordinating positions (probably due to steric reasons) as shown in (VI). These complexes, therefore, do not strictly belong to the class M(Lb)(Lt) as defined above.

Reactions of the type:

$$Ni(X-salenNR_2)_2 + Ni(X'-sal)_2 \rightleftharpoons 2 Ni(X-salenNR_2)(X'-sal)$$
 (2)

have been identified to occur in solution. The complexes on the right hand side are pentacoordinated and do belong to the class M(Lb)(Lt), X'-sal being bidentate (VII). Equilibria belonging to the type (2) has also been observed in the case of triazine-1-oxide system.

A few years ago we were attracted by the simplicity of the little used M(Lb)(Lt) strategy. We undertook a project on the synthesis, structural characterization, and reactions of new M(Lb)(Lt) species in which Lb has only oxygen donors (acetylacetone, salicylaldehyde anions or their derivatives) and Lt belongs to the type (V). The results will be summarised below. Before this is done the abbreviations used for the ligand systems are stated.

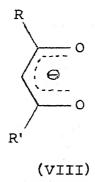
 $X'-sal \equiv structure VII, when <math>X' = H$ , X'-sal will be written as sal,

X-salenNR<sub>2</sub> = structure V, when X = H, X-salenNR<sub>2</sub> will be written as salenNR<sub>2</sub>,

 $bdk = conjugate base of \beta-diketone (structure VIII),$ 

ac = conjugate base of acetylacetone (structure VIII, R = R' = CH3),

bz = conjugate base of benzoylacetone (structure VIII, R= CH3 and R'= ${\rm C_6H_5}$ ).



### System Cu(X'-sal)(X-salNR2)

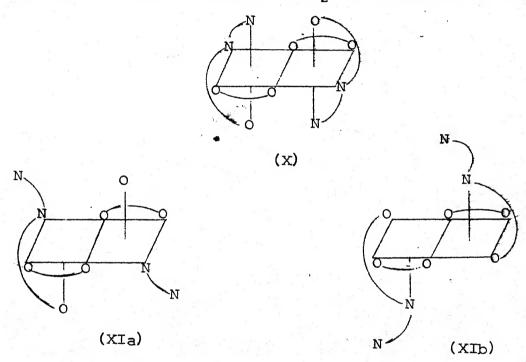
In our attempts to generate these systems, we were particularly encouraged by the report of Pfeiffer and Krebs<sup>10</sup> that  $\mathrm{Cu(sal)}_2$  reacts with N,N-diethylethylenediamine to give rise to a green complex of empirical formula  $\mathrm{Cu(sal)}(\mathrm{salenNEt}_2)$ . We have shown<sup>11,12</sup> that the reaction of  $\mathrm{Cu(X'-sal)}_2$  and N,N-diethylethylenediamine taken in the molar ratio 1:1 in toluene provides an efficient, neat and general method for the synthesis of  $\mathrm{Cu(X'-sal)}(\mathrm{X-salenNR}_2)$ . These (i) are monomolecular in solution, (ii) give rise to C=N, C=O stretches in the infrared, (iii) show two electronic bands in the region 710-580 nm,

(iv) exhibit an axial epr spectrum with  $g_{\parallel}$  ~2.06 and  $g_{\parallel}$  ~2.24. On the basis of these and other evidences it was concluded that  $Cu(X'-sal)(X-salenNR_2)$  are pentacoordinated, probably with square pyramidal geometry. This has been fully corroborated by three dimensional X-ray structural work<sup>13</sup> on  $Cu(sal)(salenNMe_2)$  (IX). The reactivity of  $Cu(X'-sal)(X-salenNR_2)$  towards acids and other reagents has been examined. 11,12

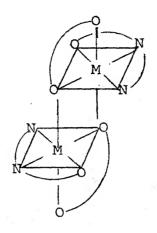
# System Ni<sub>2</sub>(sal)<sub>2</sub>(salenNR<sub>2</sub>)<sub>2</sub><sup>14,15</sup>

These dimeric species are fully paramagnetic ( $\sim 3.10$  B.M. per nickel) in the solid state and in solution over a wide range of temperature. The electronic spectrum in the solid state is characteristic of an octahedral geometry for nickel(II)( $v_1 \sim 935$  nm and  $v_2 \sim 610$  nm). Spectra in solution(benzene, chloroform) are temperature dependent due to the existence of the equilibrium

The pentacoordinated species shows a ligand field band at ~ 1335 nm, whose intensity increases with increasing temperature, showing that equilibrium (3) shifts to the right as temperature is raised. It has been proposed that the octahedral species has the structure X, while the square pyramidal could be either XIa or XIb. All the species are high-spin. It was seen earlier that Cu(sal)(salenNR<sub>2</sub>) is monomeric and square-



pyramidal. The nickel(II) dimer arises by simple stacking of two copper(II)-like monomers (IX) one above the other in a manner shown in XII, which is of course equivalent to (X). The nickel(II) species provide an example where pentacoordination in M(Lb)(Lt) is hindered by dimerisation (see Section I.2). It is known that unlike copper(II), nickel(II) has a higher affinity

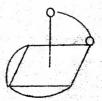


(XII)

for hexacoordinated geometry as compared to pentacoordinated geometry. The  $M(X'-sal)(X-salenNR_2)$  system provides an additional example.

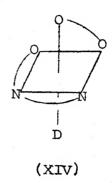
## System Cu(ac)(salenNR<sub>2</sub>)<sup>16</sup>

These are formed when [Cu(ac)(OCH<sub>3</sub>)]<sub>2</sub> and tridentate Schiff base are refluxed in 1:2 ratio in methanol. On the basis of spectral and magnetic studies Cu(ac)(salenNMe<sub>2</sub>) has been suggested to have a square pyramidal geometry both in the solid and in solution (XIII, compare with IX). On the other hand, Cu(ac)(salenNEt<sub>2</sub>) forms a pseudooctahedral methanol adduct in the solid state which looses methanol on dissolution with benzene.



(XIII)

When bis(bdk)nickel(II) (hydrated or anhydrous) (1 mol) is reacted with the Schiff base salenNR2 (1 mol) in boiling toluene and the resulting brown solution is left to crystallise in open air (which supplies moisture), shining green crystals of composition Ni(bdk)(salenNR2)(OH2) deposit (where bdk = ac or bz). Alternatively Ni(ac)(salenNR2)(OH2) can be obtained by reacting Ni(ac)2.2H2O with Ni(salenNR2)2 or Ni(salenNR2)2 with Hac in equimolecular amounts in boiling toluene followed by open air crystallisation. When heated in the range 80-100°C at 5 mm the green crystals slowly disintegrate to a brown mass which when cooled becomes a glassy solid. During this process water is lost, the maximum loss corresponding to one mole of water per mole of the complex. The composition of glassy mass is found to be  $Ni(ac)(salenNR_2)$ . When this is crystallised from moist solvents the crystals of Ni(ac)(salenNR2)(OH2) is regenerated. From solvents containing pyridine (py) crystals of Ni(ac)-(salenNR2)(py) can be readily obtained. This system is monomolecular in benzene solution. In the solid state Ni(ac)(salen- $NR_2$ )(D) (D =  $H_2$ O, pyridine) is fully paramagnetic. It is octahedral (XIV) in the solid state. On the other hand, the anhydrous species show electronic spectra characteristic of high-spin square pyramidal nickel(II) ( ${}^{3}B_{1}(F) \rightarrow {}^{3}E(F) \sim 1370 \text{ nm}; {}^{3}B_{1}(F) \rightarrow {}^{3}A_{2}(F)$  $\sim$  950 nm;  $^{3}B_{1}(F) \rightarrow ^{3}B_{2}(F) \sim$  770 nm;  $^{3}B_{1}(F) \rightarrow ^{3}E(F) \sim$  600 nm).



They belong to the structural type (XIII). In solution (benzene, chloroform) the equilibrium

is observed. On the basis of variable temperature spectral data, the thermodynamic parameters for this equilibrium have been determined to be  $\Delta H^0 = -13 \, (\pm 1) \, \text{kcal mol}^{-1}$  and  $\Delta S^0 = -38 \, (\pm 5) \, \text{eu}$ . For a given compound, the population of pentacoordinate species for a given solvent has the order benzene <chloroform nitrobenzene. In these systems, pentacoordination is hindered by adduct formation (see Section I.2).

## System Co(ac)(salenNR<sub>2</sub>)<sup>20</sup>

These are readily obtained by reacting bis(acetylacetonato)-cobalt(II) with the Schiff base in boiling toluene. On the basis of magnetic and spectral data it has been concluded that

Co(ac)(salenNEt<sub>2</sub>) belongs to the structural type XIII (square-pyramidal) both in solid state and in solution. On the other hand Co(ac)(salenNMe<sub>2</sub>) is octahedral (dimerisation, structural type X) in the solid state. But it becomes pentacoordinated in solution.

All results stated above are summarised in Table I.1.

TABLE I.1

STEREOCHEMISTRY OF M(Lb)(Lt) SYSTEMS

System	Molecu-	Stru	cture	Comments
	larity	Solid	Solution	
Cu(sal)(salenNR <sub>2</sub> )	Monomer	SP	SP	Ideal M(Lb)(Lt) system.
Ni(sal)(salenNR <sub>2</sub> )	Dimer	0	SP ⇌ O	Pentacoordina- tion partially hir dered by dimeri- sation.
Cu(ac)(salenNR <sub>2</sub> )	Monomer	spa	SP	
Ni(bdk)(salenNR <sub>2</sub> )H <sub>2</sub> O	tt .	0	$SP + H_2O$ $\rightleftharpoons O$	Adduct formation hinders pentacoordination.
Ni(bdk)(salenNR <sub>2</sub> )	u	SP	SP	
Co(ac)(salenNR <sub>2</sub> ) <sup>b</sup>	- s	P or 0	SP	Pentacoordina- tion partially hindered by di- merisation.

a, Cu(ac)(salenNEt2)CH3OH is pseudooctahedral in solid state.

b, Not soluble enough for molecular weight measurement.

SP, Square pyramidal.

O, Octahedral.

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#### CHAPTER II

### SOME PYRROLE BASED MIXED COMPLEXES

Abstract: New systems of the type M(pyrenNR2) Br, M(pyrtnNR2) Br (M = Cu, Ni), M(pyr)(pyrenNR<sub>2</sub>) (M = Cu, Ni), Cu(pyr)(pyrtnNR<sub>2</sub>)(where Hpyr is pyrrole-2-aldehyde, pyrenNR, is Schiff base of pyr and NR2CH2CH2NH2 and pyrtnNR2 is Schiff base of pyr and NR2CH2CH2CH2NH2) are reported. The first two systems are shown to have planar geometry in which pyrenNR, and pyrtnNR, act as tridentate ligands. On the basis of magnetic, spectral and X-ray powder diffraction studies on pure crystals and on solid solutions of nickel(II) and copper(II) species, it is concluded that M(pyr)(pyrenNR<sub>2</sub>) has a tetracoordinate grossly planar geometry in which the NR, group of pyrenNR, fails to occupy a coordination position due to steric overcrowding. The powder epr spectrum of Ni(pyr)(pyrenNR2) doped with the corresponding copper(II) species is axial showing both hyperfine (in parallel region) and superhyperfine (in perpendicular region) splittings. Models demonstrate that this steric difficulty mentioned above should considerably decrease on replacement of pyrenNR, by pyrtnNR, Indeed the species Cu(pyr)(pyrtnNR2) have electronic spectra strongly suggestive of pentacoordination.

<sup>\*</sup>The work described in this chapter has appeared in Inorg. Chim. Acta, 18, 257 (1976).

### II.1 INTRODUCTION

In most systems described in the last chapter the M(bidentate)(tridentate) unit shows the coordination pattern I for the bidentate and II for the tridentate ligand. In total

three oxygen and two nitrogen atoms are involved in coordination and two out of the three chelate rings are six-membered. We wanted to investigate the structural effect of making more chelate rings five membered and more coordinating atoms nitrogen. We therefore investigated the synthesis and structure of systems based on pyrrole-2-aldehyde (Hpyr) and its Schiff base with  $H_2N-(CH_2)_n-NR_2$  (n = 2 or 3). The conjugate base of these species are shown in III and IV. III will be abbreviated as pyr, while

$$(III)$$

$$N^{-}$$

$$N^{-$$

the abbreviation for IV will be pyrenNR $_2$  (when n=2) and

pyrtnNR<sub>2</sub> (when n=3). The corresponding neutral Schiff bases will be called HpyrenNR<sub>2</sub> and HpyrtnNR<sub>2</sub>.

The pyrrole-2-aldimine group (refer to IV) is a fragment of biomolecules such as porphyrins. In this regard the pyrrole-2-aldimine complexes are of peripheral biochemical interest. There are a few reports<sup>1,2</sup> on the chelates of pyrrole-2-aldimines. All of these deal with the structural type M(R-pyr)<sub>n</sub> (V) and M(pyr<sub>2</sub>B) (VI). The potentially tridentate ligand obtained by condensing Hpyr and ethanolamine gives Cu(pyr-ethanolamine) when refluxed with copper acetate in methanol.<sup>3</sup> The bis chelate of pyrrole-2-aldehyde, Cu(pyr)<sub>2</sub> is also described.<sup>4</sup> No mixed ligand species based on ligands III and IV are reported in literature (except our own work).

### II.2 RESULTS AND DISCUSSION

### A. Syntheses

The following systems have been obtained in the present work: M(pyrenNR<sub>2</sub>)Br, M(pyrtnNR<sub>2</sub>)Br, M(pyrtnNR<sub>2</sub>). Cu(pyr)-(pyrtnNR<sub>2</sub>) (M = Cu or Ni).

 $M(pyrenNR_2)$ Br and  $M(pyrtnNR_2)$ Br were obtained as dark coloured shining crystals by reacting  $(Et_4N)_2MBr_4$  with the Schiff base in presence of strong base such as potassium-t-butoxide in tetrahydrofuran (non-aqueous chelation reaction). The overall synthetic reaction is

$$(Et_4N)_2MBr_4 + HpyrenNR_2 + C_4H_9OK \longrightarrow$$

$$M(pyrenNR_2)Br + 2Et_4NBr + KBr + C_4H_9OH$$
 (1)

A similar reaction can be written for the pyrtnNR2 system.

Brown crystals of  $Ni(pyr)(pyrenNMe_2)$  were obtained by a similar nonaqueous chelation reaction involving  $(Et_4N)_2NiBr_4$ , Hpyr, HpyrenNMe<sub>2</sub> and base.

Green crystals of  $\underline{\text{Cu(pyr)(pyrenNR}_2)}$  and  $\underline{\text{Cu(pyr)(pyrtnNR}_2)}$  were obtained by aqueous reactions.

Pyrrole-2-aldimine complexes of copper(II) of type (V) are readily obtained by the following reaction in aqueous media:

$$2Hpyr + Cu^{2+} + 2RNH_2 \longrightarrow Cu(R-pyr)_2$$
 (2)

However, when RNH<sub>2</sub> is replaced by N, N-disubstituted ethylenediamine green crystals of mixed ligand complex of composition Cu(pyr)(pyrenNR<sub>2</sub>) are readily deposited. The second pyr moiety does not undergo Schiff base condensation even when excess amine is used. The observed reaction can be written as:

$$2 \text{Hpyr} + \text{Cu}^{2+} + \text{NH}_2 \text{CH}_2 \text{CH}_2 \text{NR}_2 \longrightarrow \text{Cu(pyr) (pyrenNR}_2)$$
 (3)

The mixed ligand complexes are also obtained by reacting  ${\rm Cu(pyr)}_2$  with the appropriate amine taken in 1:1 molar ratio in boiling toluene.

 $Cu(pyr)_2 + H_2NCH_2CH_2NR_2 \xrightarrow{boiling} Cu(pyr)(pyrenNR_2)$  (4)  $Cu(pyr)(pyrtnNR_2)$  can be synthesised using the same procedure. <u>B</u>. The Systems M(pyrenNR<sub>2</sub>) Br and M(pyrtnNR<sub>2</sub>) Br

Physical data are set out in Tables II.1-II.3. Representative electronic and infrared spectra are displayed in Figs. II.1 and II.2.

The nickel(II) system is diamagnetic while the copper(II) complexes have the normal magnetic moment of 1.8 BM (Table II.1). These results suggest the structure VII. The most

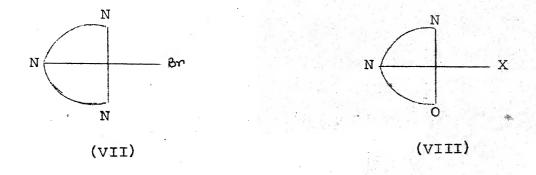


TABLE II.1

MAGNETIC SUSCEPTIBILITY DATA FOR  $M(\text{PyrenNR}_2)$  Brand and  $M(\text{PyrtnNR}_2)$  Br COMPLEXES

	Temp.		Susceptibilitya	
Compound	်ပ ၀	x <sub>g</sub> × 10 <sup>6</sup>	x <sub>M</sub> × 10 <sup>6</sup>	μ <sub>eff</sub> (ΒΜ)
Cu(pyrenNEt2)Br	30	3.46	1321	1.80
$Cu(pyrtnNMe_2)$ Br	29	3.86	1387	1.84
Ni(pyrenNMe <sub>2</sub> )Br	28		Diamagnetic	
$Ni(pyrenNEt_2)Br$	28		Diamagnetic	

 $\chi_{g}$  and  $\chi_{M}$  are gram and corrected molar susceptibilities respectively in the solid state.

important point to note here is that both the ligand systems pyrenNR2 and pyrtnNR2 act in the tridentate fashion.

Analogous systems (M(tridentate) (monodentate)) derived from some other ligands are reported in literature. 5,6-11 The properties of the present copper(II) systems are very much alike to those of salicylaldimine systems of the type Cu(səlenNR<sub>2</sub>)X with coordination sphere VIII studied by us<sup>5</sup> and others. Both systems show a prominent d-d band (Fig. II.1; Table II.3) in the region 670-600 nm. Interestingly the intensity of this band is higher in VIII (300-400) than in VII  $(\sim 150)$ . This may partly be due to lower symmetry of the coordination sphere VIII. Both Cu(pyrenNR2) Br and Cu(pyrtnNR2) Br show an intense band in the near ultraviolet (370 nm) (Table II.3 and Fig. II.1). This, and an additional band at 320 nm is also shown by the nickel species. No specific assignments have been made to these bands which may be of intraligand or metalligand origin. The electrical conductivity data (Table II.2) suggest that the compounds undergo partial dissociation (for complete dissociation, the conductivity 11 would be 75-95 ohm -1 cm<sup>2</sup> mol<sup>-1</sup>) in solution, probably <u>via</u> reactions of the type:

TABLE II.2

SELECTED INFRARED FREQUENCIES ( ${\rm CM}^{-1}$ ) AND ELECTRICAL CONDUCTIVITY<sup>a</sup> OF M(pyrenNR<sub>2</sub>)Br and M(pyrtnNR<sub>2</sub>)Br COMFLEXES

Compound	Phase	Assignment V <sub>C=N</sub>	Electrical conductivity in nitromethane \(\lambda(\text{ohm}^1\text{cm}^2\)
Cu(pyrenNEt <sub>2</sub> )Br	KBr	1590	15
$\mathtt{Cu(pyrtnNMe}_2)$ Br	Nujol mull	1610	34
$\mathtt{Ni(pyrenNMe}_2)$ Br	Nujol mull	1585	15
$\mathtt{Ni(pyrenNEt}_2)$ Br	Nujol mull	1590	19

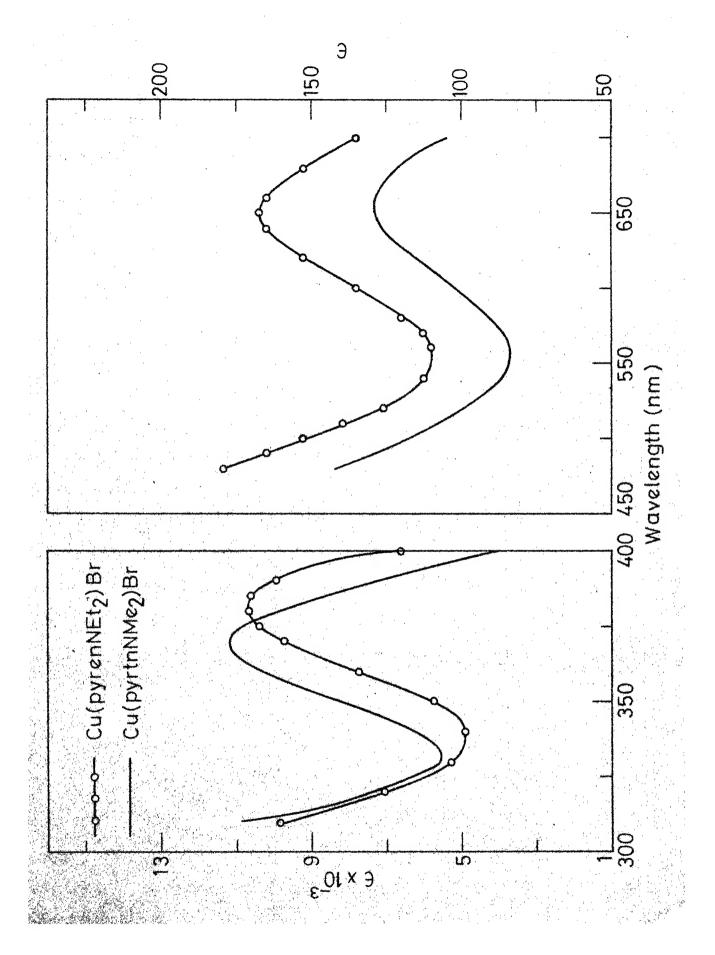
a Measurements were made at  $28^{\rm O}{
m C}$  and solute concentrations were in the range 1-3x10<sup>-3</sup> M.

TABLE II.3

ABSORPTION MAXIMA (  $\lambda$ , nm ) AND EXTINCTION COEFFICIENTS<sup>a</sup> (  $\epsilon$ , L.MOL<sup>-1</sup>.CM<sup>-1</sup>) OF ELECTRONIC BANDS OF M(pyrenNR<sub>2</sub>)Br AND M(pyrtnNR<sub>2</sub>)Br COMPLEXES AT ROOM TEMPERATURE (25-30<sup>o</sup>C)

Compound	Medium	γ (ε)
Cu(pyrenNEt <sub>2</sub> )Br	Nujol mull Toluene	620, 520sh, 410 650(168), 500sh(153), 380(10693)
Cu(pyrtnNMe <sub>2</sub> ) Br	Nujol mull Toluene	650, 530sh, 415 655(135), 360(11173)
$Ni(pyrenNMe_2)$ Br	Nujol mull Toluene	620sh, 425 580sh(178), 420(4086), 370(4917), 320(9072)
Ni(pyrenNEt $_2$ )Br	Nujol mull Toluene	620sh, 410 580sh(166), 425(5371), 370(4297), 320(7213)

<sup>&</sup>lt;sup>a</sup> Solute concentrations were adjusted (between  $2-3x10^{-3}M$ ) so as to get the optical density value in the range 0.5-1; sh is shoulder.

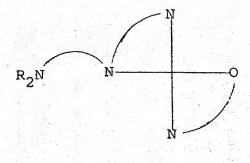


$$M(pyrenNR_2)Br + nCH_3NO_2 \rightleftharpoons$$

$$M(pyrenNR_2)(CH_3NO_2)_n^+ + Br^- \qquad (5)$$

### $\underline{\mathbf{C}}$ . $\mathbf{Cu}(\mathbf{pyr})(\mathbf{pyrenNR}_2)$ System

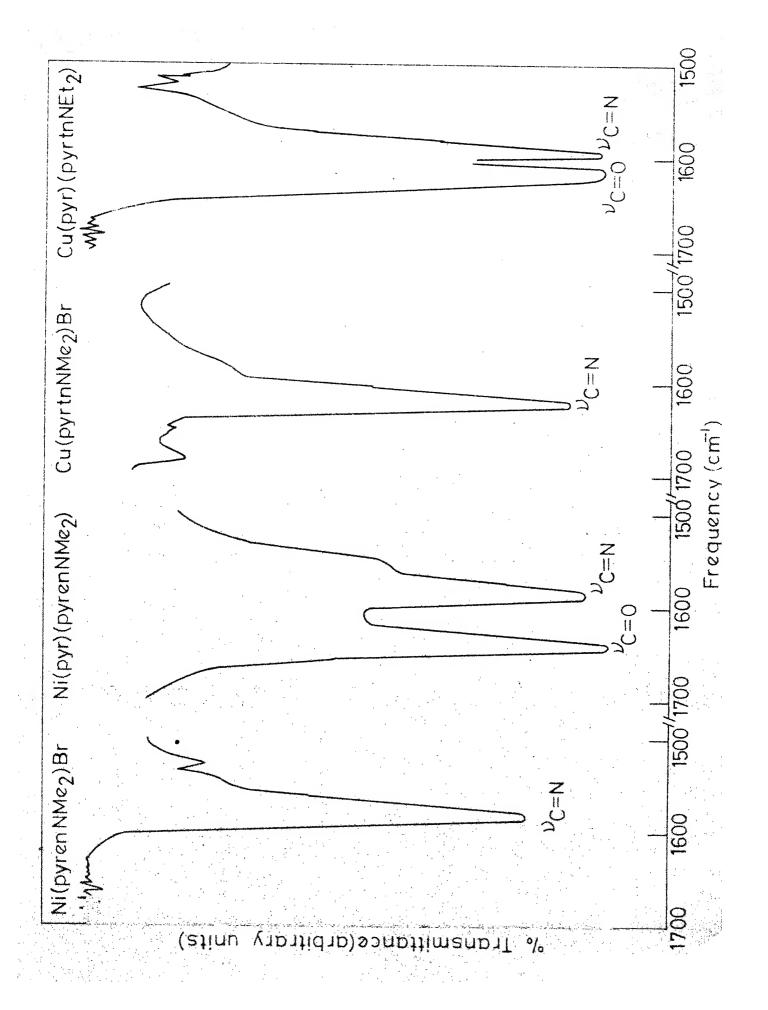
Physical data are set out in Tables II.4-II.6. We shall briefly consider the infrared results (Fable II.4, Fig. II.2) first. Cu(pyr)<sub>2</sub> shows the C=0 stretch at 1650 cm<sup>-1</sup>, while the Cu(tridentate)Br system described earlier, has the C=N stretch at 1600 cm<sup>-1</sup> (Table II.2). As expected, the mixed ligand complexes show both C=0 and C=N stretches. Cu(pyr)(pyrenNEt<sub>2</sub>) was found to be monomolecular in freezing benzene (Mol. Wt. Found: 362; Calcd: 350). The complexes could be either pentacoordinated belonging to the class M(bidentate)(tridentate) with all potential donor sites bound to the metal or tetracoordinated and planar with bidentate pyrenNR<sub>2</sub> as in IX. (NR<sub>2</sub> group is not coordinated to the metal). The systems have normal magnetic moments (Table II.5), which are of no diagnostic value for structural identification. Ligand field spectra however, throw some light on this problem. Usually pentacoordinated copper(II)



(IX)

TABLE II.4

AND Cu(pyr)(pyrtnnR <sub>2</sub> ) COMPLEXES	yr) (pyrtnNR <sub>2</sub> ) COMPLEX	ES F? Lellin . Z .	
Compound	Phase	Assignment VC=0	= \frac{1}{2}
Cu(pyr) (pyrenNMe <sub>2</sub> )	Nujol	1615	1595
$Cu(pyr)(pyrenNet_2)$	Nujol	1613	1598
$Ni(pyr)(pyrenNMe_2)$	Nujol	1640	1585
Cu(pyr)(pyrtnNMe <sub>2</sub> )	Nujol	1610	1590
$Cu(pyr)(pyrtnNet_2)$	Nujol	1605	1595



MAGNETIC SUSCEPTIBILITY DATA FOR M(Pyr) (pyrenN $_2$ ) AND Cu(pyr) (pyrtnN $_2$ ) COMPLEXES

Compound	Temp.	$x_g \times 10^6$	x <sub>M</sub> × 10 <sup>6</sup>	µ <sub>eff</sub> (BM)
Cu(pyr)(pyrenNMe <sub>2</sub> )	32	3.97	1427	1.88
$Cu(pyr)(pyrenNet_2)$	32	3.68	1421	1.88
$\tt N1(pyr)(pyrenNMe_2)$			Diamagnetic	
$cu(pyr)(pyrtnNMe_2)$	32	3.82	1445	1,88
$Cu(pyr)(pyrtnNet_2)$	32	3.88	1598	1.98
a x <sub>g</sub> and x <sub>M</sub> are gram	and corrected mo	olar suscepti	gram and corrected molar susceptibilities respectively in	ıy in

the solid state.

species give rise to two bands in the visible  $\operatorname{region}^{12,13}$  (vide  $\operatorname{supra}$ ).  $\operatorname{Cu(pyr)(pyrenNR_2)}$  shows only one band around 600 nm (Table II.6; Fig. II.3). The planar  $\operatorname{complex}^{14}$   $\operatorname{Cu(pyr)}_2$  having the  $\operatorname{Cu_2N_2O_2}$  chromophore shows a single broad ligand field transition centred at 650 nm. On the other hand complexes of the type V with planar  $\operatorname{CuN}_4$  coordination sphere show<sup>2</sup> the corresponding transition around 550 nm. The structural type IX has  $\operatorname{CuN_3O}$  coordination sphere and may be expected to give rise to a ligand field band in the intermediate range namely 650-550 nr. This is in line with experimental observation.

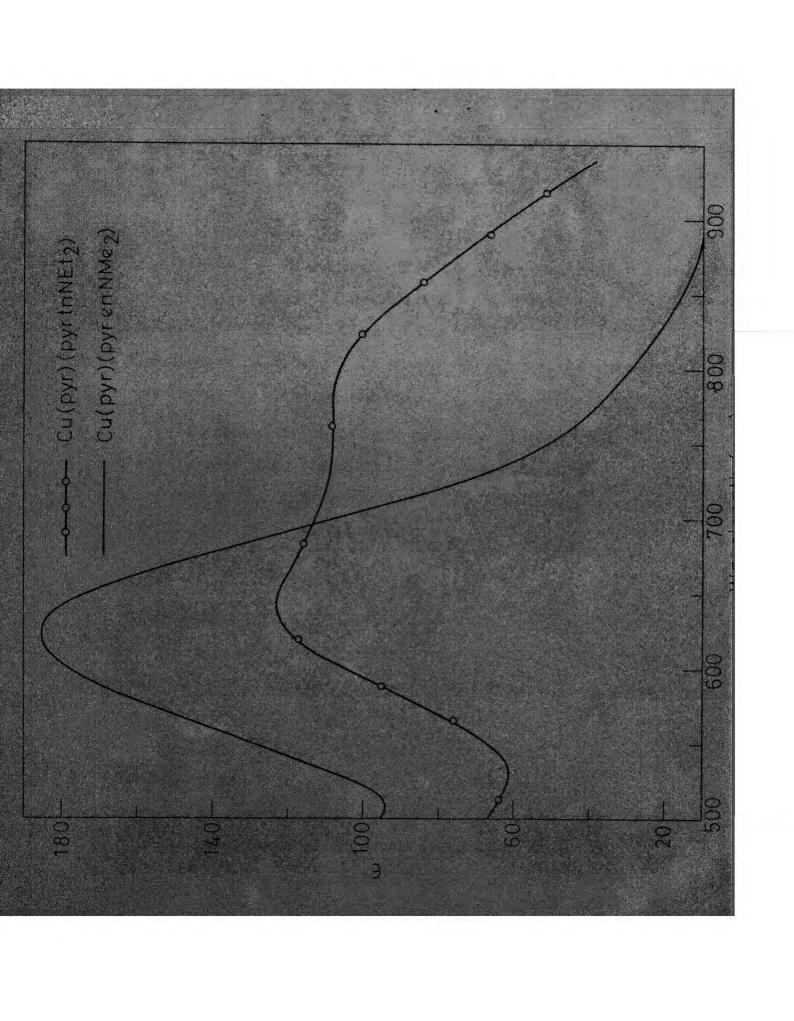
Infrared data throw some additional light supporting the structure IX. Infrared data were collected on the complex Cu(pyr)(pyrNHEt) in which substituents on the amine nitrogen of the tridentate moiety are H and Et. This complex was synthesised with the hope that N-H frequency will give us an idea about whether the terminal nitrogen is coordinated or not. The N-H stretching frequencies in secondary amines and imines fall in the range 3300-3500 cm in the absence of molecular association. The complex Cu(pyr)(pyrNHEt) gives rise to a band at 3310 cm in dichloroethane. The N-H frequency is thus not much influenced. This is an indication that NHEt nitrogen is not coordinated to the metal. In many salicylaldimine complexes where an NHR group is coordinated to a metal a lowering of the N-H stretching frequency by  $\sim 200$  cm is often observed.  $^{5,6,15}$ 

TABLE II.6

ABSORPTION MAXIMA ( $\lambda$ , nm) AND EXTINCTION COEFFICIENTS<sup>a</sup> ( $\varepsilon$ , L.MOL<sup>-1</sup>, CM<sup>-1</sup>) OF ELECTRONIC BANDS OF M(pyr) (pyrenNR<sub>2</sub>) AND Cu(pyr) (pyrtnNR<sub>2</sub>) COMPLEXES

Compound	Medium	λ(ε)
$Cu(pyr)(pyrenNMe_2)$	Nujol mull	580
	Benzene	620(186)
Cu(pyr) (pyrenNEt <sub>2</sub> )	Nujol mull	290
	Benzene	640(205)
$N1(pyr)(pyrenNMe_2)$	Nujol mull	415sh
	Benzene	410sh(176)
$Cu(pyr)(pyrtnNMe_2)$	Nujol mull	565
	Benzene	790(105), 630(135)
Cu(pyr) (pyrtnNEt <sub>2</sub> )	Nujol mull	800, 625
	Benzene	790(108), 640(123)

<sup>&</sup>lt;sup>a</sup> Solute concentrations were adjusted (between  $2-3 \times 10^{-3} M$ ) so as to get the optical density value in the range 0.5-1; sh is shoulder.



# D. Ni(pyr)(pyrenNMe<sub>2</sub>)

More definitive evidence in favour of structure IX is obtained from studies of mixed crystals of  $Cu(pyr)(pyrenNMe_2)$  and  $Ni(pyr)(pyrenNMe_2)$ . Before we proceed to describe these results, we note that the pure nickel(II) complex is monomeric in solution and is diamagnetic both in solid phase and in solution. It shows an electronic band around 410 nm, characteristic of planar  $NiN_4$  chromophore. Clearly the nickel(II) species belongs to the structural type IX, in which the  $NR_2$  (R = Me) group is not coordinated to the metal ion.

X-ray powder patterns were taken on pure copper(II) and nickel(II) complexes (Fig. II.4). The calculated d-spacings are set out in Table II.7. The two pure complexes are clearly not isomorphous with each other.

#### E. Mixed Crystals

Inspite of lack of isomorphism of the two pure complexes, mixed crystals of the two containing more than 50% Cu(pyr)(pyrenNMe<sub>2</sub>) could be readily grown from benzene. One mixed crystal system containing 56% Cu(pyr)(pyrenNMe<sub>2</sub>) and 44% Ni(pyr)(pyrenNMe<sub>2</sub>) was examined in detail. The magnetic moment of Cu(pyr)(pyrenNMe<sub>2</sub>) in this was found to be normal viz.,

1.84 ± 0.1 BM assuming that nickel(II) is diamagnetic. The electronic spectrum of mixed crystal taken in nujol mull is fully in accord. The spectrum shows a band at 600 nm

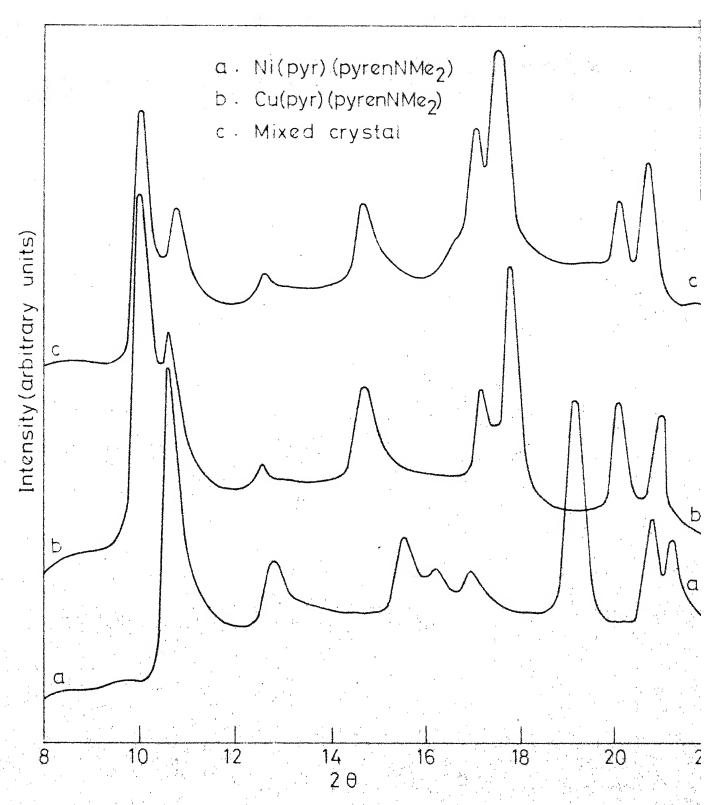


FIG. II. 4 X-RAY POWDER PATTERNS OF M(pyr)(pyrenNR2) COMPLEXES

TABLE II.7

X-RAY POWDER PATTERN DATA<sup>a</sup> OF M(pyr)(pyrenNR<sub>2</sub>) COMPLEXES

Ni(pyr)	$\mathrm{Ni}\left(\mathrm{pyr}\right)\left(\mathrm{pyrenNMe}_{2}\right)$	Cu(pyr)(	Cu(pyr)(pyrenNMe <sub>2</sub> )		Mixed	Mixed crystal
26	d-spacings	29	d-spacings		26	d-spacings
10.5	8.43	10.0	8.84		10,05	8 .82
12.8	6.92	10.6	8,35		10.8	8.19
15.5	5.72	12.6	7.03		12.6	7.03
16.2	5.47	14.7	6.03		14.7	6.03
16.9	5.25	17.2	5.16		17.0	5.22
19.15	4.63	17.8	4.98	. 0	17.6	5.04
20.8	4.27	20.1	4.42		20.1	4.42
21.1	4.21	20.85	4.26	.,	20.7	4.29
		 -				

a The first eight reflections with  $2\theta$  in the range  $10-21^{\rm O}$  are reported.

characteristic of copper(II) species and a shoulder around 420 nm due to the planar nickel(II) species (compare with results of Table II.6).

The most important observation is that the mixed crystals are isomorphous with pure Cu(pyr)(pyrenNMe<sub>2</sub>), as determined from X-ray powder patterns and d-spacings (Table II.7; Fig. II.4). Since nickel(II) is diamagnetic and planar (IX) in the mixed crystal, it follows that the copper(II) species has also the geometry IX in the mixed crystal. Because of isomorphism, this is also true for the pure copper(II) complex. We thus conclude that Cu(pyr)(pyrenNMe<sub>2</sub>) has the planar environment IX. The lack of isomorphism of pure copper(II) and nickel(II) complexes must arise from different packing of otherwise structurally very similar molecules.

The epr spectrum of a very dilute solution of Cu(pyr)(pyrenNMe<sub>2</sub>) in Ni(pyr)(pyrenNMe<sub>2</sub>) (such solutions have of
course the structure of the latter pure complex) was examined
in the powder form at room temperature. The spectrum is displayed in Fig. II.5. This is an axial spectrum with a so-called
extra line<sup>15a,15b</sup> in the perpendicular region. A spectrum computer-simulated with parameters

$$g_{||} = 2.199 ; A_{||} = 187.0 Gauss$$
  
 $g_{||} = 2.045 ; A_{||} = 6.0 Gauss.$ 

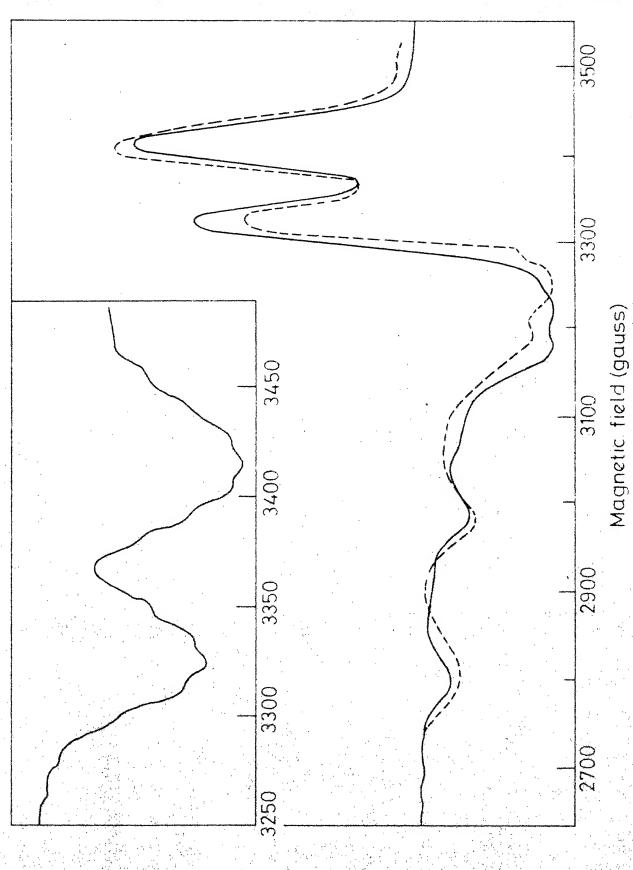


FIG II S POWDER EPR SPECTRA OF MIXED CRYSTAL OBSERVED SPECTRUM (-

fits very well with the experimental spectrum (Fig. II.5). The width of Lorentzian lines (of which the observed is an envelope) were taken as 50G and 40G for parallel and perpendicular regions respectively. I am thankful to Mr. S. Baral of this laboratory for his assistance in Computer simulation. Rich superhyperfine splittings are observed in expanded spectra in the perpendicular (but not in the parallel) region (inset in Fig. II.5) due the existence of spin density on nitrogen binding sites and possibly adjacent hydrogen atoms. <sup>15c</sup> No further analysis of the superhyperfine structure was made. We hope to do so from single crystal epr data which are now being collected.

In Chapter I (Section I.2), we have categorised the various ways in which pentacoordination may be hindered in a M(bidentate) (tridentate) system. The pyrrole-2-aldimine species described above, provides an example where the potentially tridentate unit, actually acts only as a bidentate ligand (vide structure III, Chapter I). In the next section, we examine why this happens so.

#### F. Steric Factors

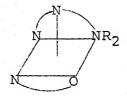
It is firmly established<sup>5,16</sup> that  $Cu(sal)(salenNR_2)(X$ , sal; XI, salenNR<sub>2</sub>) has the square pyramidal structure XII. In view of this and in view of the observation that in  $M(pyrenNR_2)$  pyrenNR<sub>2</sub> is tridentate, it is pertinent to examine why pyrenNR<sub>2</sub> fails to use  $NR_2$  coordination in  $M(pyr)(pyrenNR_2)$ . We strongly

suspect that the phenomenon is of steric origin. Like salenNR<sub>2</sub> in XII and other structures,  $^{17}$  pyrenNR<sub>2</sub> in its tridentate mode will be able to span only in the meridional fashion due to the short length of the  $-(CH_2)_2$ — chain. Models show that this brings the bidentate pyr moiety unfavourably close to the methyl groups of NMe<sub>2</sub> in pyrenNMe<sub>2</sub> in the hypothetical square pyramidal structure XIII:

This steric hindrance leads to the delinking of NMe<sub>2</sub> from the metal atom. In XII, the benzene ring of sal is situated one bond (O-C) away from the corner of the basal plane and also the chelate ring is six-membered. Models clearly demonstrate that steric interaction between sal and NR<sub>2</sub> is virtually absent.

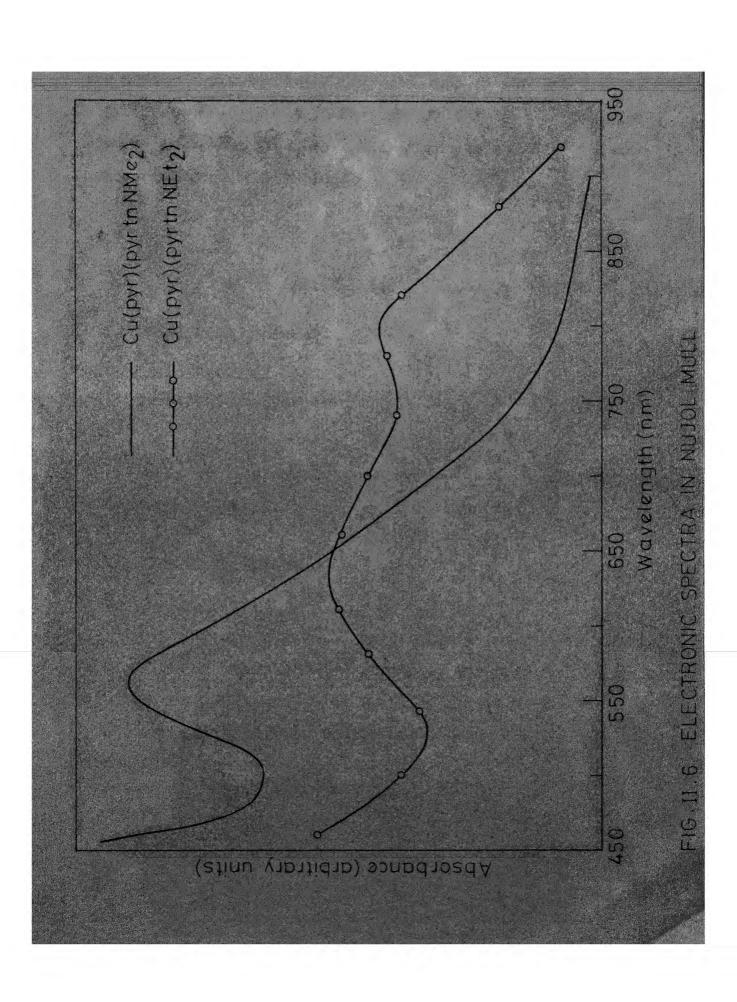
# G. Pentacoordination in Cu(pyr)(pyrtnNR2)

If the above thesis regarding the steric effect in M(pyr)(pyrenNR<sub>2</sub>) is correct, the complexes  $Cu(pyr)(pyrtnNR_2)$  with a
more flexible  $-(CH_2)_3$ — chain may be pentacoordinated. In this
potentially tridentate ligand can span facially. Models show
that the configuration XIV is free from steric strain:



(XIV)

With the above ideas in mind these complexes were synthesised by using methods analogous to those used for Cu(pyr)(pyren-NR<sub>2</sub>). The complex Cu(pyr)(pyrtnNEt<sub>2</sub>) was found to be monomolecular in freezing benzene (Mol. wt., Found: 369; Calcd: 364). They have normal magnetic moments and infrared spectra (Table II.5 and II.3), and two distinct electronic bands in visible region (Fig. II.3). This spectrum is very much alike to that of Cu(sal)(salenNR<sub>2</sub>) system. It is thus strongly suggestive of pentaccordination. In idealised C<sub>4v</sub> geometry, the d-orbital order is d<sub>xz,yz</sub> < d<sub>xy</sub> ~ d<sub>z</sub> < < d<sub>x<sup>2</sup>-y<sup>2</sup></sub>. The two observed bands can be assigned as d<sub>xy</sub>, d<sub>z</sub>  $\rightarrow$  d<sub>x<sup>2</sup>-y<sup>2</sup></sub>, 790 nm; d<sub>xz</sub>, d<sub>yz</sub>  $\rightarrow$  d<sub>x<sup>2</sup>-y<sup>2</sup></sub> 640 nm. Interestingly, the spectrum of Cu(pyr)(pyrtnNMe<sub>2</sub>) in the solid state (one band 565 nm) (Fig. II.6) is very different



from that in solution but is closely akin to the spectrum of Cu(pyr)(pyrenNR<sub>2</sub>) (Table II.6). The former complex thus provides an important link being planar in the solid state and pentacoordinated in solution.

#### II.3 EXPERIMENTAL SECTION

#### A. Preparation of Compounds

#### a. Starting Chemicals

Pyrrole-2-aldehyde was synthesised as described in literature.  $^{18}$ 

The N, N-dialkylethylenediamines and N, N-dialkylpropylenediamines were obtained from Aldrich Chemical Co., U.S.A.

## b. Preparation of Complexes

#### i. Schiff Bases

Pyrrole-2-aldehyde (0.01 mol) and the appropriate amine (0.01 mol) were taken in 20 ml ethanol. The solution was heated to reflux for 0.5 hr. Alcohol was then stripped on a rotary evaporator. The resulting Schiff base (brown liquid) was used without further purification.

# ii. Cu(pyr)<sub>2</sub>

 ${
m Cu(pyr)}_2$  was prepared from pyrrole-2-aldehyde and basic carbonate of  ${
m Cu(II)}$  as described in literature.

# iii. $M(pyrenNR_2)Br$ and $M(pyrtnNR_2)Br$

To a solution of Schiff base (0.01 mol) in 40 ml dry tetrahydrofuran, was added potassium t-butoxide (0.01 mol) followed by  $(\text{Et}_4\text{N})_2\text{MBr}_4$  (0.01 mol). The mixture was magnetically stirred for about 6 hr. During this period the solution became dark brown (M=Ni) or dark green (M=Cu). This was filtered and the residue was extracted several times with toluene. The toluene extract on concentrating gave dark coloured crystals. These were recrystallised from toluene. The yield was 50%.

# iv. Cu(pyr)(pyrenNR2) by Aqueous Reaction

Excess of appropriate amine was added to 0.02 mol of pyrrole-2-aldehyde and 0.01 mol of CuSO<sub>4</sub>.5H<sub>2</sub>O dissolved in 50 ml water. The solution was heated on a steam bath. After cooling to room temperature, 2 ml of 5% NaOH was added.

In the case of Cu(pyr)(pyrenNMe<sub>2</sub>), the precipitated material was filtered and then extracted with ethanol-dichloromethane mixture. The extract was concentrated and cooled. Dark green crystals thus obtained were collected by filtration and recrystallised from dichloromethane.

In the case of Cu(pyr)(pyrenNEt<sub>2</sub>) a green substance started depositing on the walls of the reaction vessel. When deposition was complete the aqueous portion was removed by decantation. The residue was dissolved in benzene and was dried over anhydrous sodium sulphate. The solution was then concentrated and hexane was added. A gum separated. On standing for several days in air, the gum slowly transformed to microcrystals of the required complex. They were collected by filtration and were washed by hexame. The yield was 35%.

# v. Cu(pyr)(pyrenNR<sub>2</sub>) and Cu(pyr)(pyrenNHEt) in Nonaqueous Medium

o.02 mol of Cu(pyr)<sub>2</sub> and 0.02 mol of the appropriate amine were taken in 40 ml of toluene and the mixture was heated to reflux for 1 hr. The mixture was then filtered and its volume was reduced to 10 ml. 10 ml of hexane was then added. Green crystals separated out on cooling. These were collected by filtration and recrystallised from toluene-hexane mixture. The synthesis in non-aqueous medium is more convenient than the synthesis in aqueous medium.

# vi. Cu(pyr)(pyrtnNR<sub>2</sub>)

These were prepared by procedures similar to those used for Cu(pyr) (pyrenNR2).

# vii. Ni(pyr)(pyrenNMe2)

A nonaqueous chelation reaction of pyrrole-2-aldehyde ( $\mathbb{Q}$ .01 mol), pyrenNMe<sub>2</sub> (0.01 mol), potassium-<u>t</u>-butoxide (0.02 mol) and (Et<sub>4</sub>N)<sub>2</sub>NiBr<sub>4</sub> (0.01 mol) in tetrahydrofuran using a procedure entirely analogous to that used for (M(pyrenNR<sub>2</sub>)Br gave dark brown crystals of composition Nf(pyr)(pyrenNMe<sub>2</sub>).

#### viii. Mixed Crystal

The mixed crystals were prepared as follows. A benzene solutions of Cu(pyr)(pyrenNMe<sub>2</sub>) (0.01 mol) and Ni(pyr)(pyrenNMe<sub>2</sub>) (0.01 mol) were mixed. This was heated on steam bath. Slow evaporation of the solution yielded dark coloured mixed crystals.

The composition of the crystals were determined using the band intensity at 620 nm (Table II.6) as an index of the concentration of the copper(II) complex. The mixed crystals were found to have 56% Cu(pyr)(pyrenNMe<sub>2</sub>) and 44% Ni(pyr)(pyrenNMe<sub>2</sub>). The yield was 50%.

### B. Characterization of Complexes

#### a. C, H, N Analyses

These were done by microanalytical methods. Characterization data for all complexes are collected in Table II.8.

#### b. Gravimetric Estimation of Copper

The complexes were decomposed by heating with concentrated HNO $_3$  (5 ml) and then with concentrated HCl till the brown fumes ceased to appear. After cooling,50 ml of water was added and the solution was neutralised with 5% NaOH till a little of white precipitate formed. To this 1 ml of conc.  $\rm H_2SO_4$  and 15 ml of 5% sodium bisulphite solution were added. The solution was heated nearly to boiling and 10 ml of 10%  $\rm NH_ASCN$ 

PABLE II.8

CHARACTERIZATION DATA FOR M(pyrenNR<sub>2</sub>) Br, M(pyrtnNR<sub>2</sub>) Br, M(pyr) (pyrenNR<sub>2</sub>) and Cu(pyr) (pyrtnNR<sub>2</sub>) complexes

				. 4						
יני מנינטעשט יני מנינטעשט	6 0 cm	%	ر %د	%	·H%	%	N%	W %	q l	
primodilion	) 'du	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
Cu(pyrenNEt2)Br	127-128	39.34	39,50	5.41	5.56	12.56	12,30	18.91	18.77	
$Cu(pyrenNMe_2)Br$	150-151	37.32	37,35	5.01	5.12	13.11	12.80	19.74	19.59	
Ni(pyrenNMe $_2$ )Br	216-217	35.67	35.22	4.66	4.31	13,92	13.80	19.37	19.50	
$Ni(pyrenNet_2)Br$	141-142	39.92	39.73	5.49	5.58	12.74	12.70	17.72	17.85	
$Cu(pyr)(pyrenNMe_2)$	157-158	52.24	52.36	5.64	9.00	17.41	17.30	19.74	19.79	
$Cu(pyr)(pyrenNet_2)$	112-113	54.92	54.99	6.34	6.53	16,01	15.97	18.16	17,95	
${\rm Ni}({\rm pyr})({\rm pyrenNMe}_2)$	189-190	53.00	53.02	5.72	5.80	17.73	17.60	18.51	18.50	
$Cu(pyr)(pyrtnNMe_2)$	180-181	53.64	53.75	9	5.84	16.68	16,88	18.92	18.97	
$Cu(pyr)(pyrtnNet_2)$	113-114	56.10	56.35	6.65	6.75	15,39	15,53	17.46	17.46	
			'3							

a All melting points are uncorrected.

b Copper was estimated as CuBCN and nickel as dimethylglyoximate.

solution was added with stirring. It was allowed to stand for 4 hr. after which it was filtered through G-4 sintered crucible. The residue was dried at 110°C and weighed as CuSCN.

### c. Gravimetric Estimation of Nickel

Accurately weighed (100 mg) compound was taken in a coni-It was decomposed by heating on a hot plate with conc. HNO2 (twice with 5 ml portions) 10 ml of conc. HCl was added and the mixture was heated to boil till the brown fumes ceased to evolve being replaced by white fumes. After cooling to room temperature 15-20 ml of water was added. Usually some insoluble material separated out on the surface of the faint green solution which was then filtered through sintered funnel. sintered funnel was given a repeated wash by distilled water. The volume of the filtrate and washings together increased to 100 ml. The solution was heated on a steam bath and slight excess of dimethylglyoxime (1% solution in 95% ethanol; calculated on the basis of 1 ml per 2 mg of nickel) was added. alkaline with ammonia (a little in excess). The red precipitate was digested on steam bath for 2-3 hr. It was then filtered through a preweighed sintered crucible. The precipitate was washed with 20% ethanol till free from chloride. It was dried at 110-120°C for 2 hr, cooled in a desiccator and weighed to constant weight as bis(dimethylglyoximato)nickel(II).

#### C. Solvents

Tetrahydrofuran was kept over fused calcium chloride for 12 hr. Then it was heated to reflux over sodium wire in presence of benzophenone till the colour became deep blue. It was distilled and used immediately. Benzene was purified by successive shaking with concentrated sulphuric acid (to remove thiophene), sodium bicarbonate solution and water. The solvent was then dried over fused calcium chloride and was finally distilled over sodium. Nitromethane was kept over anhydrous sodium sulphate and was distilled just before use. The middle fraction (boiling point 101°C) was collected. Toluene was distilled over sodium. Dichloromethane and other solvents required for recrystallisation were taken straight from bottles of British Drug House AnalaR quality or equivalent.

#### D. Physical Measurements

#### a. Infrared Spectra

These were recorded on a Perkin-Elmer 531 recording spectrophotometer either in nujol mull, as KBr pellets or in solution.

#### b. Electronic Spectra

These were measured on a Cary-14 recording spectrophotometer. Solid samples were examined in finely dispersed hydrocarbon mulls sandwitched between quartz plates. Silica cells

of path length (1-2 cm) were used depending on the concentration of solutions and intensities of bands.

#### c. Molecular Weight

Molecular weights were determined in carefully purified benzene using the cryoscopic procedure in presence of sodium sulphate. 19

#### d. Electrical Conductance Measurements

These were measured on a Systronics (India) conductivity bridge using a platinised conductivity cell with a cell constant  $= 0.548 \text{ cm}^{-1}$ .

## e. Bulk Susceptibility Measurements

These were carried out using a sensitive Gouy balance 20 assembled by Dr. T.S. Kannan and Dr. S. Gupta of this laboratory. The unit consists of a Varian V-4005 electromagnet (pole caps tapered to one inch diameter) a matching V-2900 solid state power supply and an Ainsworth semimicro balance. The current fed to the magnet could be regulated to carry out variable field measurements. All measurements were carried out over a wide range of field strengths.

Split sample tubes were used for all measurements on solids. Either  ${\rm CoHg(SCN)_4}^{21}$  or  ${\rm CuSO_4.5H_2O}$  was used as the standard. From the observed weight differences, the susceptibility of the sample was calculated using standard equations,  $^{22}$ 

The diamagnetic correction for the ligands and metal ion was made on the basis of Pascal's constants given by Selwood. 22

### f. Magnetic Susceptibility of Mixed Crystal

The gram susceptibility (  $\chi_{\rm g}$ ) observed for the mixed crystal can be written as

$$(x_q)_{mc} = f_{Cu}(x_q)_{Cu} + f_{Ni}(x_q)_{Ni}$$
 (6)

where  $f_{Cu}$  and  $f_{Ni}$  are respectively the weight fraction of the copper(II) and nickel(II) complexes and ( $\chi_g$ )<sub>Cu</sub> and ( $\chi_g$ )<sub>Ni</sub> are the respective gram susceptibilities. We have  $f_{Cu}$  = 0.56;  $f_{Ni}$  = 0.44; ( $\chi_g$ )<sub>Ni</sub> = 0.47x10<sup>-6</sup> cgs units (calculated from Pascal's constants). ( $\chi_g$ )<sub>mc</sub> is found to be 2.04x10<sup>-6</sup> cgs units. Using Eqn. (.6) we get ( $\chi_g$ )<sub>Cu</sub> = 4.00x10<sup>-6</sup> cgs units and hence ( $\chi_M$ )<sub>Cu</sub> (corrected for diamagnetism) = 1437. This yields  $\mu_{eff}$  for copper(II) in the mixed crystal as 1.84 BM.

## g. X-Ray Powder Pattern

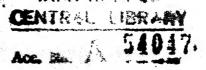
These data were collected on a GE XRD-6 Diffractometer with  $\text{CuK}\,\alpha$  radiation.

#### h. Electron Spin Resonance Spectra

The powder epr spectra were recorded on a Varian V-4502 EPR Spectrometer operating at the X-band frequency (9.5 GHz). The Zeeman field at the site of the sample inside the cavity was modulated by 100 KHz frequency modulation. Diphenylpicrylhydrazyl(DPPH) (g = 2.0036) was used as the standard field marker.

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#### CHAPTER III

DIMERIC MIXED COMPLEXES WITH NICKEL(II)\*

Abstract: By reacting trimeric bis-(acetylacetonato)nickel(II) with tridentate Schiff bases derived from salicylaldehyde and N,N-dialkyl-1,3-diaminopropylenediamine, new dinuclear mixed ligand species of the type Ni<sub>2</sub>(bidentate)<sub>3</sub>(tridentate) have been obtained. The probable structure of such species is described on the basis of various physicochemical data. Nickel(II) has octabled environment in these complexes.

<sup>\*</sup>The work described in this chapter has appeared in Ind. J. Chem., 14A, 785 (1976).

#### III.1 INTRODUCTION

In our search for the pentacoordinated species of the type Ni(bidentate)(tridentate), the reaction of bis(acetyl-acetonato)nickel(II), Ni<sub>3</sub>(ac)<sub>6</sub> with HsalenNR<sub>2</sub> was investigated earlier (Chapter I). Square pyramidal species of the type Ni(ac)(salenNR<sub>2</sub>) were thus obtained. Having observed the dramatic stereochemical consequence of the -(CH<sub>2</sub>)<sub>n</sub>-chain length in pyrrole-2-aldimine complexes (Chapter II), we undertook the investigation of the effect of this chain length on the composition and stereochemistry of some nickel(II) species. The systems obtained by reacting Ni<sub>3</sub>(ac)<sub>6</sub> with saltnNR<sub>2</sub> (I) are reported in this chapter. The properties of the species obtained are compared with those of Ni(ac)(salenNR<sub>2</sub>).

#### III.2 RESULTS AND DISCUSSION

## A. Syntheses

Three Schiff bases of the type I were prepared (R=Me, Et, and Bu). By reacting the Schiff base (0.1 mol) with  $Ni_3(ac)_6$ 

(0.07 mol) in toluene green crystals of composition  $Ni_2(ac)_3$  - (saltnNR<sub>2</sub>) are readily obtained.

The observed molecular weights are in line with the above formulation (Table III.1).

## B. Physical Data and Structure

All the complexes show an ir band (Fig. III.1 and Table III.1) in the region 1620-1630 cm $^{-1}$  assigned to  $^{\nu}_{\rm C=N}$  of the Schiff base moiety. There are two strong bands at 1590 cm $^{-1}$  and 1510 cm $^{-1}$  which are due to the combination of  $^{\nu}_{\rm C=-C}$  and  $^{\nu}_{\rm C=-O}$  stretches of ac with additional contributions from aromatic vibrations of the Schiff base.

The complexes are fully paramagnetic both in the solid state and in chloroform solution (Tables III.2 and III.3). In the visible region the complexes show two bands at 1170 nm and  $\sim$ 640 nm (Fig. III.2 and Table III.4). The bands are weak and are clearly of ligand field origin. The spectrum suggests pseudooctahedral nickel(II) stereochemistry. The two bands can be readily assigned as:  $^3A_{2g} \rightarrow ^3T_{2g}$ , 1170 nm;  $^3A_{2g} \rightarrow ^3T_{1g}(F)$ ,  $\sim$ 640 nm.

On the basis of model building it is proposed that Ni<sub>2</sub>(ac)<sub>3</sub>-(saltnNR<sub>2</sub>) has the structure II in which ac occupies bridging positions. It is known that the dinuclear fragment is coordinatively unsaturated and yields adducts such as Ni<sub>2</sub>(ac)<sub>4</sub>(pyridine) in which nickel(II) is octahedral. One may then expect

TABLE III.1

SELECTED INFRARED FREQUENCIES  $(CM^{-1})$  AND MOLECULAR WEIGHT DATA<sup>a</sup> OF  $Ni_2(ac)_3(saltnnR_2)$  COMPLEXES

Compound		Assignment	nt	Molecular weight	weight
	VC=N	"CO + VC	VC==-O + VC===C + Varomatic	Calcd	Found
Ni <sub>2</sub> (ac) <sub>3</sub> (saltnNMe <sub>2</sub> )	1623	1591, 1508	1508	620	009
$\operatorname{Ni}_2(\operatorname{ac})_3(\operatorname{saltnNet}_2)$	1627	1591,	1509	ସା	
$\mathrm{Ni}_2(\mathrm{ac})_3(\mathrm{saltnNBu}_2)$	1628	1593,	1508	704	675

a Molecular weights were determined cryoscopically in purified dry benzene.

b Measurement not done.

57

TABLE III.2

MAGNETIC SUSCEPTIBILITY<sup>a</sup> OF  $\mathrm{Ni}_2(\mathrm{ac})_3(\mathrm{saltnNR}_2)$  COMPLEXES IN SOLID STATE

Compound	Temperature $^{ m C}_{ m C}$	$x_g \times 10^6$	$x_{M} \times 10^{6}$	$\mu_{ ext{eff}}^{ ext{(BM)}}$
$\operatorname{Ni}_2(\operatorname{ac})_3(\operatorname{saltnNMe}_2)$	27	13.6	4356	3.24
$\mathtt{Ni}_2(\mathtt{ac})_3(\mathtt{saltnNEt}_2)$	22	12.7	4295	3.22
$\mathrm{Ni}_2(\mathrm{ac})_3(\mathrm{saltNBu}_2)$	27	11.6	4271	3,21
a $\chi_{_{\! G}}$ and $\chi_{_{\! M}}$ are gram and corrected molar susceptibilities respectively in the	and corrected molar	susceptibilities	respectively	in the

..g ... solid state per nickel atom.

TABLE III.3

MAGNETIC SUSCEPTIBILITY<sup>a</sup> DATA FOR  $\mathrm{Ni}_2(\mathrm{ac})_3(\mathrm{saltnNR}_2)$  COMPLEXES IN CHLOROFORM

Compound	Temperature oc	x <sub>g</sub> x 10 <sup>6</sup>	x <sub>M</sub> × 10 <sup>6</sup>	μ <sub>eff</sub> (BM)
$\mathrm{Ni}_2(\mathrm{ac})_3(\mathrm{saltnNMe}_2)$	20	13.75	4402	3.21
$\operatorname{Ni}_2(\operatorname{ac})_3(\operatorname{saltnNEt}_2)$	22	12.76	4295	3.20
$\mathrm{Ni_2(ac)_3(saltnNBu_2)}$	20	12.73	4510	3.26

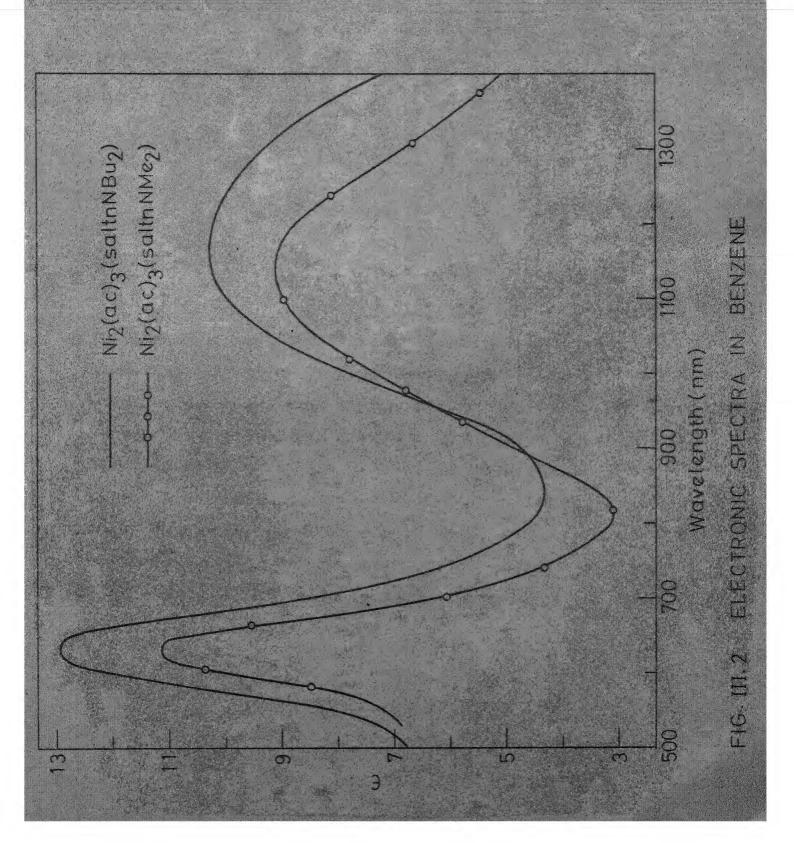
 $\chi_g$  and  $\chi_M$  are gram and corrected molar susceptibilities respectively per nickel atom. ro

TABLE III.4

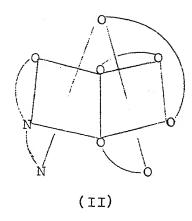
ABSORPTION MAXIMA (  $\lambda$ , nm) AND EXTINCTION COEFFICIENTS<sup>a</sup> ( $\epsilon$ , L.MOL<sup>-1</sup>CM<sup>-1</sup>) OF ELECTRONIC BANDS OF Ni<sub>2</sub>(ac)<sub>3</sub>(saltnnR<sub>2</sub>) COMPLEXES IN BENZENE

λ(ε)	1,170(9) 635(11)	1,170(10), 635(14)	1,170(10), 650(13)
Compound	$\mathrm{Ni}_2(\mathrm{ac})_3(\mathrm{saltnNMe}_2)$	$\mathrm{Ni}_2$ (ac) $_3$ (saltnNEt $_2$ )	$\mathrm{Ni}_2(\mathrm{ac})_3(\mathrm{saltnNBu}_2)$

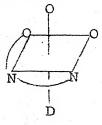
a Solute concentrations were adjusted  $(4-5 \times 10^{-3} \, \mathrm{M})$  so as to get the optical density value in the range 0.5-1.0. Extinction coefficients are per nickel atom.



that species of the type  $\mathrm{Ni_2(ac)_3(tridentate)}$  with octahedral nickel(II) should exist. The  $\mathrm{Ni_2(ac)_3(saltnNR_2)}$  system provides an example:



We have noted earlier that the reaction of  $\mathrm{Ni_3(ac)_6}$  with salenNR<sub>2</sub> yields mononuclear pentacoordinated Ni(ac)(salenNR<sub>2</sub>).<sup>3</sup> No evidence for dinuclear species has been obtained with this ligand. The difference in the behaviour of salenNR<sub>2</sub> and saltnNR<sub>2</sub> can be rationalised on the basis of structure II. In this structure saltnNR<sub>2</sub> occupies three facial positions of an octahedron. The flexible  $-(\mathrm{CH_2})_3$ - chain makes this possible.<sup>4</sup> On the other hand salenNR<sub>2</sub> can only span in meridional positions<sup>5</sup> (as in structure III) due to relative shortness of the  $-(\mathrm{CH_2})_2$ -chain, It cannot span facially.



(III)

#### III.3 EXPERIMENTAL SECTION

#### A. Preparation of Compounds

#### a. Starting Chemicals

Salicylaldehyde was obtained from Bush and Co., London.

The N,N-dialkylpropylenediamines were obtained from Aldrich Chemical Co., U.S.A.

<u>Acetylacetone</u> was obtained from British Drug House, England.

#### b. Preparation of Complexes

## i. Synthesis of bis(acetylacetonato)nickel(II)

A solution of acetylacetone (0.25 mol) in 50 ml methanol was added while stirring to a solution of NiCl<sub>2</sub>.6H<sub>2</sub>O (0.125 mol) in water. To the resulting mixture was added a solution of 0.25 mol of sodium acetate in 75 ml water. The mixture was heated briefly on a hot plate. After allowing it to attain the room temperature, it was further cooled in the refrigerator for 6-8 hr. The blue green crystals of bis(acetylacetonato)-nickel(II) dihydrate<sup>6</sup> were filtered off on a buchner funnel, washed with water and methanol. The dihydrate thus obtained was dried at 80° (5 mm) for 7-8 hr to yield deep green anhydrous compound.

## ii. SaltnNR<sub>2</sub>

The Schiff base was prepared by heating to reflux (0.5 hr) salicylaldehyde and the amine in equimolar proportions in ethanol. The solvent was removed on a rotary evaporator. The resulting brown liquid was used without further purification.

# iii. Ni<sub>2</sub>(ac)<sub>3</sub>(saltnNR<sub>2</sub>)

The Schiff base (0.1 mol) and Ni<sub>3</sub>(ac)<sub>6</sub> (0.07 mol) were taken in 75 ml toluene. The réaction mixture was heated to reflux for 1 hr. The green solution was then filtered and cooled. Hexane was added to initiate crystallisation where needed. The green complex was obtained in 50% yield.

## B. Characterization of Complexes

This was done by C, H, N, microanalysis and metal analysis. Characterization data for all complexes are collected in Table III.5.

The procedure for nickel analysis was the same as that described in Chapter II.

#### C. Solvents

Details are given in Chapter II.

#### D. Physical Measurements

#### a. Infrared Spectra

Details are given in Chapter II.

TABLE III.5

CHARACTERIZATION DATA FOR  $\operatorname{Ni}_2(\operatorname{ac})_3(\operatorname{saltnNR}_2)$  COMPLEXES

Comporting	ر 0 لا		U	H %	H		N	/0	q.w
	O dis	- 1	Calcd. Found	Calcd.	Calcd. Found	Calcd. Found	Found	Calcd.	Calcd. Found
	, -								
$Ni_2(ac)_3(saltnNMe_2)$	201	52.30 52.28	52,28	80.9	6.08	4.52	4.17 18.93	18,93	18,97
( ##Nutten) (ne) in		( ( (	! !						
2, 2, 2, 3, 3, 5, 5, 111, 1, 2, 2,	101	53.75	54.25	6.53	6.50	4.32	4.41	18.12	18,31
( " ( a) ( a) + N	7		(	: : :	*				
2,700,3,000,000,000	2	07.00	20.30	7.15	96•9	3.97	4.06	16.67	16.58

a All melting points are uncorrected.

b Nickel was estimated as dimethylglyoximate.

#### b. Electronic Spectra

Details are given in Chapter II.

#### c. Molecular Weight

Details are given in Chapter II.

#### d. Bulk Susceptibility Measurements

- (i) Details of measurements on solid samples are given in Chapter II.
- (ii) Solution measurements were made using split sample tubes. Distilled oxygen free water was used as a standard. The gram susceptibility of chloroform was found to be  $-0.05 \times 10^{-6}$  at  $25^{\circ}$ C.

The densities of solutions were determined with a suitably designed specific gravity bottle.

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#### CHAPTER IV

STRUCTURE OF NICKEL(II) AND IRON(II)
COMPLEXES OF 2-PHENYLAZOPYRIDINE\*

Abstract: 2-Phenylazopyridine (pap) acts as an unsymmetrical bidentate chelating ligand. The tris species Ni(pap)<sub>3</sub><sup>2+</sup> and Fe(pap)<sub>3</sub><sup>2+</sup> are isolated in the form of perchlorate and iodide respectively. The complex cations have pseudooctahedral geometry. From the ligand field spectrum of paramagnetic Ni(pap)<sub>3</sub><sup>2+</sup>, Dq of pap is calculated to be 1080 cm<sup>-1</sup>, a value which is close to that of ethylenediamine in Nien<sub>3</sub><sup>2+</sup> but is considerably less

<sup>\*</sup>The work described in this chapter has appeared in Ind. J. Chem.,  $\underline{14}$ A, 166 (1976).

than that of chelating diimines, such as pyridinalimine. isoelectric relationship between the diimine and azoimine fragments is noted. Fe(pap) 3 + shows an intense band in the visible region which is assigned to charge transfer from metal  $t_{2\alpha}$ (idealised  $\mathrm{O_h}$ ) to ligand  $\pi^\star$  orbital. That the charge transfer state has contribution to the ground state is also evident from The N=N stretch is considerably lowered in Fe(pap)32+ in comparison to those in the ligand and in Ni(II) complexes. The paramagnetic mixed complexes Ni(pap) $_{2}^{X}$ ,0.5CH $_{2}^{C1}$  (X = C1, Br) and diamagnetic Ni(pap)2 are reported. On the basis of magnetic, electrical conductivity and electronic spectral data. it is suggested that Ni(pap) 2X2,0.5CH2Cl2 has pseudooctahedral Ni(II) with dichloromethane held in the crystal lattice but not influencing the Ni(II) environment in any major manner.  $\text{Ni(pap)}_2\text{I}_2$  the two ligands are believed to be held in a planar manner.

#### IV.1 INTRODUCTION

In this and the next chapter, we present our work an metal (Ni, Fe) complexes obtained from ligands containing an azo group. An azo group suitably linked to an aromatic ring carrying additional donor sites is well suited for closure of a chelate ring. Good examples of such a situation are provided by the metal complexes of arylazophenols whose chelating activity has been known for many years. A phenyl azo group attached to the 2-position of a pyridine ring as in 2-phenyl-azopyridine (I) may be expected to give stable metal chelates. This problem is explored for the first time in this chapter. Some related studies recently reported in literature are those on more complex systems such as 2,2'-, 3,3'- and 4,4'-azopyridines. The coordination chemistry of these ligands is often complicated by the formation of ligand and/or anion bridging.

#### IV.2 RESULTS AND DISCUSSION

#### A. General Consideration

The ligand (I) which will be abbreviated as pap, is obtained in relatively poor yield by the reaction:  $^{7}$ 

The ligand readily reacts with Ni(II) salts yielding complexes of the type Ni(pap) $_3$ (ClO $_4$ ) $_2$ , Ni(pap) $_2$ X $_2$ , 0.5CH $_2$ Cl $_2$ (X = Cl, Br) and Ni(pap) $_2$ I $_2$ . In the crystalline state Ni(pap) $_3$ (ClO $_4$ ) $_2$  is green while the other species are dark coloured. In dichloromethane or chloroform solution the respective colours are: Ni(pap) $_3$ (ClO $_4$ ) $_2$ , green; Ni(pap) $_2$ X $_2$ , 0.5CH $_2$ Cl $_2$ , brownish green and Ni(pap) $_2$ I $_2$ , brown. The dark coloured crystals of Fe(pap) $_3$ I $_2$  obtained by direct reaction between ferrous sulphate heptahydrate and the ligand (followed by the addition of potassium iodide) readily dissolve in water to yield deep blue solutions which are not very stable.

#### B. Tris Complexes

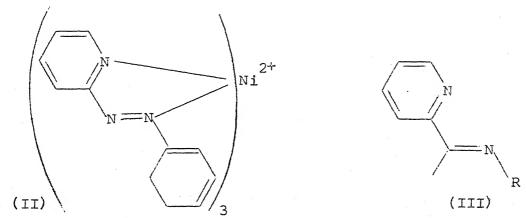
Electrical conductivity data are set out in Table IV.1. The observed values for  $\text{Ni(pap)}_3(\text{ClO}_4)_2$  and  $\text{Fe(pap)}_3\text{I}_2$  falls within the range<sup>8</sup> (150-160) expected for 1:2 electrolyte. Clearly the complex cation  $\text{M(pap)}_3^{2+}$  is present in these species.

TABLE IV.1

LELECTRICAL CONDUCTIVITY DATA IN NITROMETHANE

		Concentration	<b>V</b> .
	၁၀	mol.lit 1	$ohm^{-1}cm^2mol^{-1}$
$\operatorname{Ni(pap)}_3(\operatorname{ClO}_4)_2$	24	1.36 x 10 <sup>-3</sup> M	175
$Fe(pap)_3I_2$	19	1.86 x 10 <sup>-3</sup> M	141
$Ni(pap)_2Cl_2, 0.5CH_2Cl_2$	19	1.19 x 10 <sup>-3</sup> M	ത
$^{ m Ni(pap)}_{ m 2^{Br}_2}$ , 0.5 $^{ m CH}_{ m 2^{Cl}_2}$	19	$1.31 \times 10^{-3} \text{M}$	16
$^{ m Ni(pap)}_{ m 2}^{ m I}_{ m 2}$	19	0.93 x 10-3 M	45

 $\mathrm{Ni(pap)}_3(\mathrm{ClO}_4)_2$  is fully paramagnetic (Table IV.2). In the electronic spectrum three bands are observed in the visible region (Fig. IV.1; Table IV.3). These bands can be readily assigned on the basis of a gross octahedral geometry (coordinative positions as shown in II) for the cation  $\mathrm{Ni(pap)}_3^{2^+}$ . The



assignment is  ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ , 920 nm;  $\rightarrow {}^1E(D)$ , 855 nm and  $\rightarrow$   ${}^3T_{1g}(F)$ , 610 nm. The  ${}^3A_2 \rightarrow {}^3T_{1g}(P)$  transition is hidden under intense absorption in the uv. Since the energy of the  ${}^3A_{2g} \rightarrow$   ${}^3T_{2g}(F)$  transition is equal to 10 Dq, the Dq value of pap, is calculated to be 1080 cm $^{-1}$ . Interestingly this Dq value is considerably lower than that of 2-pyridinalimine (III) (Dq = 1250 cm $^{-1}$ ) which is isoelectronic with pap. Evidently the azomethine is a stronger donor than the azo nitrogen. Infact the 10 Dq value of Ni(pap) $_3^{2+}$  is close to that of Ni(ethylenediamine) $_3^{2+}$ .

Fe(pap) $_3$ I $_2$  is diamagnetic at room temperature. The metal atom thus has a low-spin d $^6$  configuration. The most characteristic feature of the electronic spectrum of Fe(pap) $_3$ I $_2$  (Fig. IV.2;

TABLE IV. 2

MAGNETIC SUSCEPTIBILITY DATA

Fe(pap) $_{3}I_{2}$ 22 Ni(pap) $_{3}(Clo_{4})_{2}$ 27.5		~g^ to Mx10	X <sub>M</sub> ×10 <sup>6</sup> µ <sub>eff</sub> (BM)
(0104)2	Diamagnetic	ľ	I
	4.46	4014	3.12
Ni(pap) <sub>2</sub> Cl <sub>2</sub> ,0,5CH <sub>2</sub> Cl <sub>2</sub> 22	6.74	3963	3 • .05
$Ni(pap)_2Br_2,0.5CH_2Cl_2$ 22	5.92	4090	3.10
$Ni(pap)_2I_2$	Diamagnetic	Ī	i

 $\chi_{g}$  and  $\chi_{M}$  are corrected gram and molar susceptibilities.

σ

TABLE IV.3 a, b

ABSORPTION MAXIMA ( $\lambda$ ,nm) AND EXTINCTION COEFFICIENTS ( $\epsilon$ , L. MOL<sup>-1</sup>, CM<sup>-1</sup>) OF SOME ELECTRONIC BANDS

Compound	Medium	γ(ε)
Fe(pap) $_3$ I $_2$	Water	590(5150); 550(3850)sh; 380(16900)sh;
$Ni(pap)_3(clo_4)_2$	Solution (dichloro- methane)	920(12); 855(15)sh; 610(355); 325(38130)
Ni(pap) <sub>2</sub> Cl <sub>2</sub> ,0.5CH <sub>2</sub> Cl <sub>2</sub>	Solution (chloro- form)	1150(13); 605(122)sh; 445(510); 320(2390).
	Solid	1060; 610sh; 430.
$^{ m Ni(pap)}_2{^{ m Br}}_2$ , 0.5 $^{ m CH}_2{^{ m Cl}}_2$	Solution (chloro- form)	1150(16); 590(202)sh; 440(1240)sh; 340(2825).
	Solid	1070; 615sh; 410sh.

a sh = Shoulder.

b The ligand pap shows bands at 445 and 340 nm.

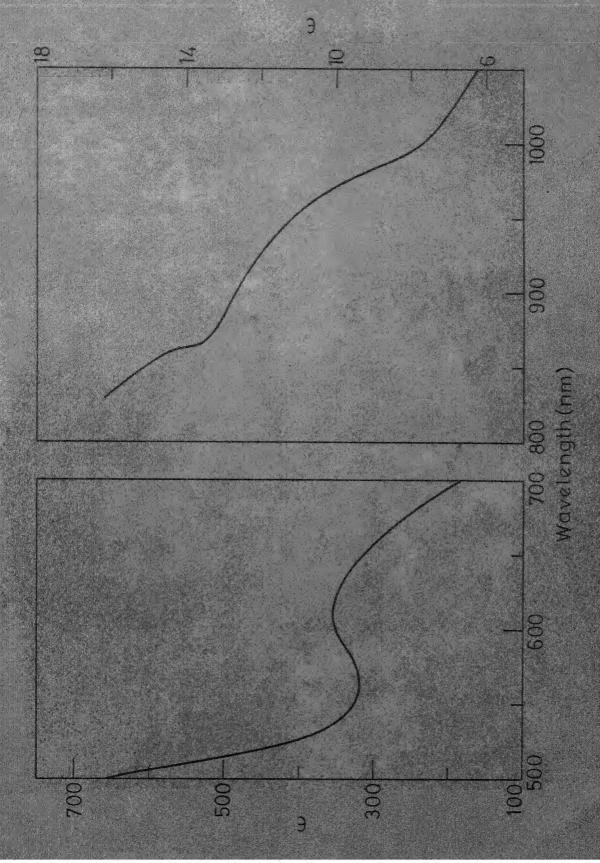


FIG. IV.1 - ELECTRONIC SPECTRUM OF NI(pap)3(ClO4)2 IN DICHLOROMETHANE

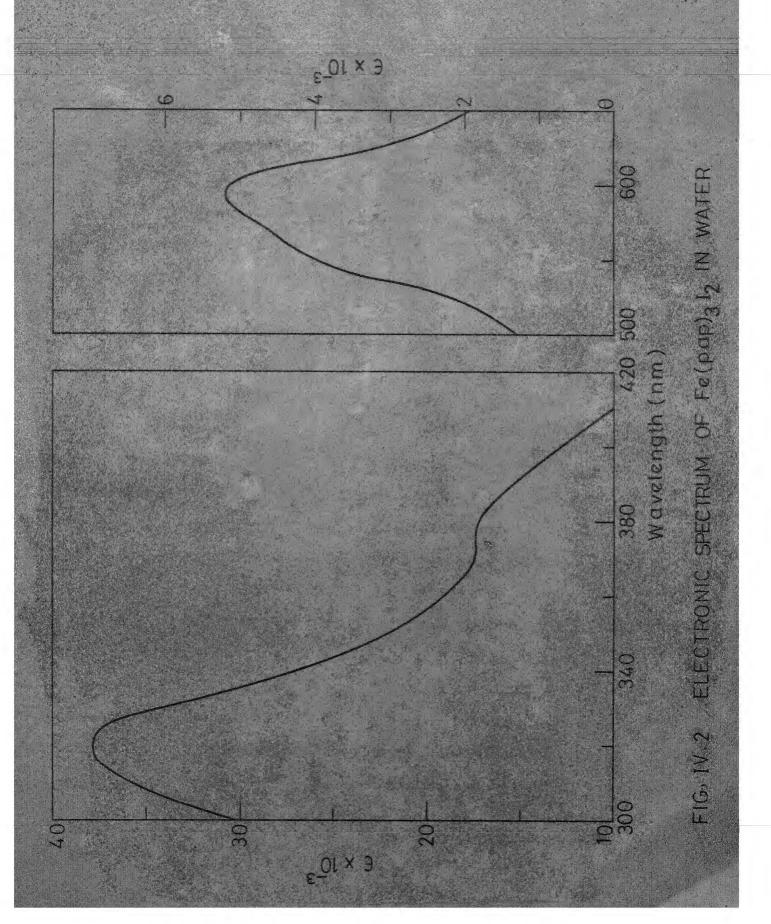


Table IV.3) is an intense band in the visible region near ~590 nm; there is a shoulder at slightly higher energy (550 nm). It is well known that tris diimine complexes of iron(II) (structural type IV), show an allowed charge transfer transition from metal

 $t_{2\sigma}$  orbital (idealised  $O_h$ ) to lowest antibonding empty diimine  $\pi^*$  orbital. 9-12 This transition is seen in the form of a band at ~ 555 nm associated with a shoulder at slightly lower energ-The shoulder is believed to be the first member in a vibrational progression (coupling with C=C + C=N vibrations). The azoimine group -N=N-C=N- as present in pap is isoelectronic with the diimine function -N=C-C=N-. Consequently low energy metal-to-ligand charge-transfer transition may be expected in Fe(pap) 2 + also. Indeed the 590 nm band in the latter complex is undoubtedly due to such a transition. We note that the metalto-ligand transition in Fe(pap)32+ is at considerably lower energy than that in Fe(diimine) 3 +. The higher Dq value (vide supra) of diimine ligand (IV) compared to the azoimine pap, may be partly responsible for this. Fe(pap)32+ also shows a band at 380 nm. The origin of this band is not certain; the ligand itself has

absorption in this region (Table IV.3).

The infrared spectra of nickel(II) and iron(II) complexes were examined. Selected results are set out in Table IV.4. Our present concern is in the -N=N- stretching frequency. This frequency and in the ligand and in Ni(pap) that and in other nickel(II) complexes described later fall in the narrow range 1418-1431 cm<sup>-1</sup>. On the other hand there is a dramatic decrease in this frequency to 1353 cm<sup>-1</sup> in Fe(pap) that are five fig. IV.3). This is evidently due to some contribution of the metal-to-ligand charge transfer state( as discussed earlier) to the ground level as in the case of Fe(diimine) that are five fig. IV.3 that is the case of Fe(diimine) that the five fig. IV.3 that is the nickel(II) species. But the effect is not as pronounced as for the azo stretch. The ligand orbital involved in charge transfer evidently has a large proportion of azo character.

# C. Structure of Ni(pap) $_2X_2$ , 0.5CH $_2$ Cl $_2$ (X = Cl, Br)

TABLE IV.4 a, b

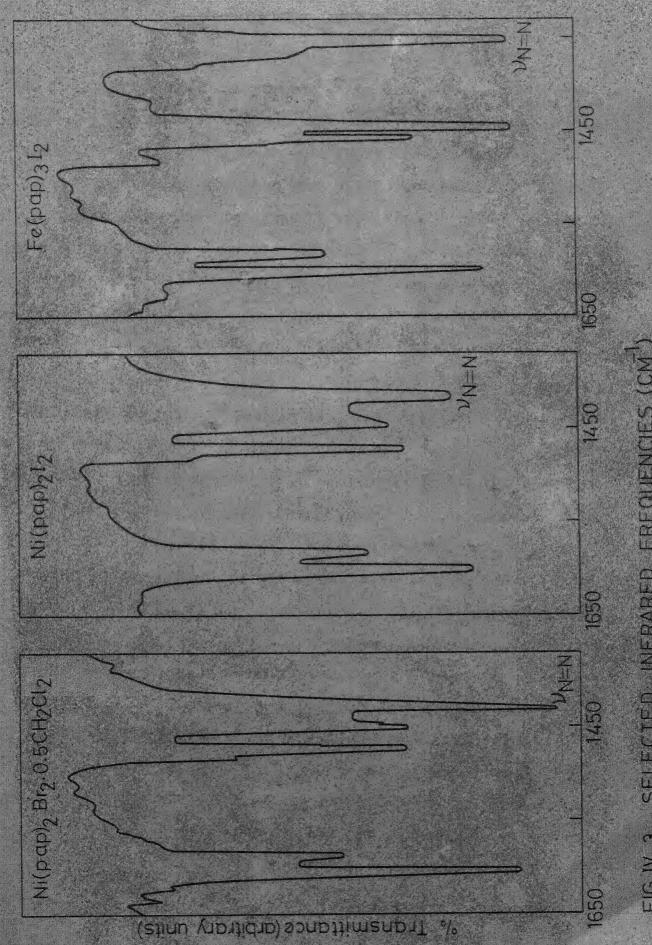
SELECTED INFRARED FREQUENCIES (CM<sup>-1</sup>)

Assignment	đeđ	Fe(pap) <sub>3</sub> 1 <sub>2</sub>	<sup>c</sup> 3 Ni(pap) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	$Ni(pap)_2Cl_2$ , d $0.5CH_2Cl_2$	Ni(pap) <sub>2</sub> Br <sub>2</sub> , d o.5CH <sub>2</sub> Cl <sub>2</sub>	Ni(pap) <sub>2</sub> <sup>1</sup> 2
Aromatic	1616(s)	1599(s)	1605(s)	1605(s)	1604(s)	1600(s)
C=C & C=N	1587 (m)	1579(m)	1586 (m)	1586 (m)	1587 (m)	1582(m)
	1477(m)	1458(m)	1484 (m)	1472(m)	1468(m)	1468(m)
	1456(s)	1446(s)	1446(s)	1452(m)	1446 (s)	1447(s)
N=N	1425(s)	1353(s)	1428(s)	1431(s)	1426(s)	1418(s)
C-H out-of- plane bend- ing in phenyl ring	687 (s)	692(s)	691(s)	698(s)	692(s)	692(s)
C-H out-of- plane bend- ing in pyri- dine ring	784(s)	772(s)	770(s)	773(s)	765 (s)	770(s)

in all compounds a. An unassigned band of medium intensity appears in the range  $740-750~{\rm cm}^{-1}$  studied. All spectra are run in KBr discs.

c.  $v_3$  of  ${
m ClO}_4$  is observed as a broad band of high intensity centred at 1100 cm  $^{-1}$ b. Symbols in parentheses refer to relative intensity; s, strong; m, medium.

<sup>1.</sup> C-Cl stretch of  $\mathrm{CH_2Cl_2}$  is at 726  $\mathrm{cm^{-1}(m)}$ .

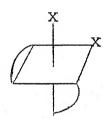


SELECTED INFRARED FREQUENCIES (CM FIG.IV.3

contain dichloromethane of crystallisation are known. We wish to stress that the present compounds can also be prepared as amorphous powders without the dichloromethane of crystallisation. On the other hand, well-formed crystals which are easy to purify are obtained when dichloromethane is present. The solid state infrared spectra of Ni(pap)<sub>2</sub>Br<sub>2</sub> and Ni(pap)<sub>2</sub>Br<sub>2</sub>, O.5CH<sub>2</sub>Cl<sub>2</sub> were found to be essentially superimposable except that the latter compound shows bands characteristic of dichloromethane also. The dichloromethane of crystallisation does not appear to affect the ligand disposition in any major way.

Considerable interest has been shown in recent years about the stereochemistry of complexes of the type  $\mathrm{Ni(Lb)}_2\mathrm{X}_2$  where Lb is a bidentate ligand. There is evidence that when X is widely separated form Lb in the spectrochemical series, the cis configuration is preferred over the trans structure. Good examples are  $\mathrm{Ni(phen)}_2\mathrm{X}_2$ ,  $\mathrm{Ni(en)}_2\mathrm{X}_2^{16}$  (dimer) and  $\mathrm{Ni(po)}\mathrm{X}_2^{17}$  where phen = o-phenanthroline, en = ethylenediamine, po = 2-pyridinal-oxime and X = Cl, Br, I. In going from  $\mathrm{NiN}_6$  to trans- $\mathrm{NiN}_4\mathrm{X}_2$ , the octahedral  $\mathrm{^3A}_{2g} \rightarrow \mathrm{^3T}_{2g}(\mathrm{v_1})$  band shows observable splitting due to decrease of symmetry from  $\mathrm{O_h}$  to  $\mathrm{D_{4h}}$ . A good example is trans- $\mathrm{Ni(py)}_4\mathrm{Br}_2$ . The cis- $\mathrm{NiN}_4\mathrm{X}_2$  sphere has a lower symmetry ( $\mathrm{C_{2v}}$ ) than trans- $\mathrm{NiN}_4\mathrm{X}_2$  but the magnitude of orbital splitting is expected to be less. In practice such splitting is often not observed. The complexes of 2-phenylazopyridine under discussion shows an unsplit  $\mathrm{v_1}$  band at 1070 nm (solid) or at

1150 nm (solution) (Fig. IV.4). Previously we have noted that 2-phenylazopyridine and ethylenediamine have similar ligand field strengths. In this context it is significant that  $v_1$  of solid Nien<sub>2</sub>Cl<sub>2</sub> (dimer) is at 980 nm, <sup>17</sup> a value which is very close to that of the presently synthesised Ni(pap)<sub>2</sub>Cl<sub>2</sub>. However, Ni(pap)<sub>2</sub>Cl<sub>2</sub> unlike the ethylenediamine complex cannot be dimeric, in view of the electrical conductivity data (vide supra). On the basis of above discussion we propose that Ni(pap)<sub>2</sub>X<sub>2</sub> has dtructure V. Far infrared studies could throw important light on this problem. Unfortunately, we do not have facilities for obtaining ir spectra below 250 cm<sup>-1</sup>.



(V)

### D. Ni(pap)<sub>2</sub>I<sub>2</sub>

This is diamagnetic and shows no ligand field bands below 700 nm. In this complex the Ni(pap)<sub>2</sub> sphere is grossly planar presumably with a <u>trans</u> (steric over crowding of phenyl groups in <u>cis</u> geometry) disposition of ligand molecules (VI). The iodide ions seems to remain partially bound (weak axial coordination) in solution, since the observed electrical conductivity

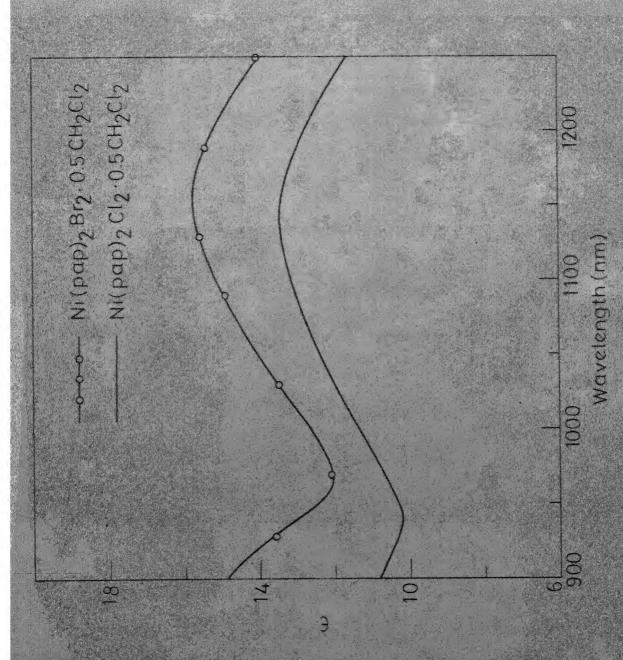


FIG. IV. 4 ELECTRONIC SPECTRA OF NI(pap)2 X2.0.5CH2Cl2 IN CHLOROFORM

is much lower than that expected for a 1:2 electrolyte. In view of the proposed difference in stereochemistry of  $Ni(pap)_2$  fragment in the chloro (or bromo) and iodo complexes, it may be significant that the -N=N- stretch in former (no centre of symmetry) is more intense than that of the latter (centre of symmetry).

#### IV.3 EXPERIMENTAL SECTION

- A. Preparation of Compounds
- a. Starting Chemicals
- i. <u>Nitrosobenzene</u> was synthesised as described in the literature. 20
- ii. 2-Aminopyridine was obtained by British Drug House, England.
- iii. Preparation of 2-phenylazopyridine: 7 5.1 g of 2-aminopyridine was added to a warm 50% NaOH solution (50 ml). The mixture was gently heated after adding a little benzene (3 ml). 6 g of

nitrosobenzene was added slowly. The entire mixture was extracted several times with benzene. The dark brown solution was boiled with charcoal and filtered. The filtrate was concentrated under reduced pressure to 25 ml. The concentrate was subjected to column chromatography, eluting it with benzene. The lower most layer (green and dirty brown) was discarded. The orange band was collected. The evaporation yielded reddish needles of 2-phenylazopyridine. It should be noted that the yield of this preparation was very poor (30%). Often the orange liquid did not solidify, which was used as such for the preparation of complexes.

#### b. Preparation of Complexes

### i. Ni(pap) 3 (Clo<sub>4</sub>) 2

A solution of Ni(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O (0.001 mol) in methanol was added to a solution of pap (0.003 mol) in the same solvent. The colour of the reaction mixture turned dark-green. The mixture was kept overnight at room temperature. The dark green crystals formed were filtered, washed with little methanol and dried (5 mm, 80°C). The yield was 50%.

### ii. Fe(pap)3I2

An aqueous ethanolic solution containing FeSO<sub>4</sub>.7H<sub>2</sub>O (0.001 mol) and pap (0.003 mol) was warmed and to this concentrated potassium iodide solution was added. On cooling to 5°C, violet crystals were deposited. These were recrystallised from water

containing dissolved potassium iodide. The yield was 60%.

### iii. Ni(pap)<sub>2</sub>Cl<sub>2</sub>,0.5CH<sub>2</sub>Cl<sub>2</sub>

A methanolic solution of NiCl<sub>2</sub>.6H<sub>2</sub>O (0.001 mol) was added to a methanolic solution of the ligand (0.002 mol). The solvent was removed by heating on a steam-bath. The resulting gum was extracted with dichloromethane. The extract was concentrated and cooled to room temperature. A dark coloured crystalline solid deposited which was then recrystallised from dichloromethane. The crystals analysed as Ni(pap)<sub>2</sub>Cl<sub>2</sub>,O.5CH<sub>2</sub>Cl<sub>2</sub>, yield was 50%.

## iv. Ni(pap) 2Br2, 0.5CH2Cl2

The bromo compound was prepared using the above procedure starting from NiBr2.

## $v. Ni(pap)_{2}^{X}_{2} (X = Cl. Br)$

When chloroform was used as the solvent for extracting the gum in the above preparations dark-green amorphous powder of composition  $\text{Ni(pap)}_{2}^{X}$  were obtained. The chloroform does not enter the lattice, unlike dichloromethane.

# vi. Ni(pap) 2 12

A methanolic solution containing  $Ni(CH_3COO)_2.4H_2O$  (0.001 mol) and ligand (0.002 mol) was gently warmed. Potassium iodide

solution was then added to this mixture. The dark solid thus obtained yielded dark crystals(brown when powdered) on recrystalisation from chloroform-hexane mixture. Yield was 60%.

#### B. Characterization of Complexes

This was done by C, H, N microanalysis and metal analysis. Characterization data for all complexes are collected in Table IV.5.

The procedure for nickel analysis was the same as described in Chapter II.

#### Iron Estimation

100 mg of sample was taken in a conical flask and 5 ml of conc. HNO<sub>3</sub> was added. The mixture was heated to boil. Brown fumes started evolving. When the brown fumes subsided, 10 ml of HCl was introduced and the mixture was again heated to boil. A clear pale yellow solution was obtained. The heating was continued to evaporate almost all the cacid. 25 ml of water was added. An aqueous ammonia solution was then added dropwise, till a faint brownish precipitate persisted, which was dissolved by adding minimum quantity of 1N HCl. Then 1.5 g of ammonium acetate in 70 ml water was added followed by oxine solution (2 per cent in N-acetic acid) from a burette with constant stirring until a slight excess was present. About 6-7 ml was required. The dark precipitate thus obtained was digested on a water bath for 1 hr,

TABLE IV.5

CHARACTERIZATION DATA

7	%	% C	%	Н%	%	. N%	% N	% Metal
	Calcd	Calcd Found	Calcd	Calcd Found	Calcd	Calcd Found	Calcd	Found
$Fe(pap)_3I_2$	46.10 46.35	46.35	3,14 3,43	3.43	14.66	14.66 14.79	6.50	6.45
$\operatorname{Ni(pap)}_{3}\left(\operatorname{ClO}_{4}\right)_{2}$	49.00	49.28	3,37	3,52	15,60	15,80	7.27	7.10
Ni(pap) $_2$ Cl $_2$ ,0.5CH $_2$ Cl $_2$ a	48:70	48.43	3.36	3,21	15.49	15.24	10,82 10,60	10,60
Ni(pap) <sub>2</sub> Br <sub>2</sub> ,0.5CH <sub>2</sub> Cl <sub>2</sub> <sup>b</sup>	42.47	42.26	2.89	3.02	13.04	13,15	9,11	9.23
N1 (pap) $_2\mathrm{I}_2$	38.88	38.43	2.65	2.86	12.37	12.43	8,65	8.84

a. The percentage of chloride directly bound to nickel, Calcd: 13.07; Found: 12.72. b. The percentage of bromide directly bound to nickel, Calcd: 24.80; Found: 24.90.

filtered through a preweighed sintered crucible, washed successively with 1% acetic acid and water. It was dried in hot air oven at 125-135 $^{\circ}$ C to constant weight. It was weighed as Fe(C<sub>6</sub>H<sub>6</sub>OH)<sub>3</sub>.

#### C. Solvents

Details are given in Chapter II.

#### D. Physical Measurements

#### a. Infrared Spectra

Details are given in Chapter II,

#### b. Electronic Spectra

Details are presented in Chapter II,

#### c. Bulk Susceptibility Measurements

Details of measurements of solid samples are available in Chapter II.

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#### CHAPTER V

#### MIXED METAL COMPLEXES OF ARYLAZOOXIMES

Abstract: Arylazooximes (R-C(=NOH)-N=N-Ar) abbreviated as Haao, have the azoimine fragment which strongly binds iron(II) giving rise to five-membered chelate rings (ir data). The tris chelate  $Fe(aao)_3^-$  is green in colour due to the presence of a strong metal  $\rightarrow$  ligand charge transfer transition at  $^{\circ}600$  nm. This ion can be isolated in the form of the sodium salt  $NaFe(aao)_3^-$ .  $H_2O$  in which,  $Fe(aao)_3^-$  has <u>cis</u> geometry (pmr data). The sodium ion is believed to be bound to the water molecule and to oxime oxygen atoms.  $NaFe(aao)_3^-$ .  $H_2O$  is poorly conducting in nitromethane solution. It is soluble in a variety of organic solvents including benzene. On reaction with acid it produces  $HFe(aao)_3^-$  in

which the proton is believed to be chelated (intermolecularly or intramolecularly) to Fe(aao) via the oxime oxygen atoms. Reaction of Haao with FeCl3 produces a crystalline solid which has been shown to be an intervalence species of the type  $[Fe^{III}(Fe^{II}(aao)_3)_2]Fe^{III}Cl_4$  ( 1:1 electrolyte in nitromethane and nitrobenzene). In this both iron(III) atoms are high-spin. The iron(III) atom in the cation is most probably bound in an octahedral fashion to the six oximato oxygen atoms of two cis-Fe(aao) moieties. The presence of Fe-O and Fe-Cl stretches has been identified in the infrared region. The corresponding perchlorate [Fe<sup>III</sup>(Fe<sup>II</sup>(aao)<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> is obtained by a direct reaction between iron(II) perchlorate and Haao. The chemical interconversion of the various species viz., NaFe(aao)3.H2O,  $\mathrm{HFe(aao)_3}$ ,  $\mathrm{[Fe(Fe(aao)_3)_2]FeCl_4}$  and  $\mathrm{[Fe(Fe(aao)_3)_2]ClO_4}$  are described. For example [Fe(Fe(aao)3)2]FeCl4 reacts with sodium hydroxide to yield two moles of NaFe(aao), H2O and two moles of iron(III) hydroxide. On the other hand NaFe(aao)3.H2O reacts with one mole of FeCl3 to regenerate [Fe(Fe(aao)3)2]FeCl4. The species [Fe(Fe(aao) $_3$ ) $_2$ ]Br and Ni[Fe(aao) $_3$ ] $_2$  are briefly described. [Fe(Fe(aao)<sub>3</sub>)<sub>2</sub>]X (X = ClO<sub>4</sub>, Br) shows a g'  $\sim 4.3$  epr line characteristic of rhombic FeO sphere. When X = FeCl4, an intense additional band at g ~ 2.0 (due to FeCl<sub>4</sub>) is also observed.

#### V.1 INTRODUCTION

In this chapter mixed arylazooxime complexes of sodium(I), iron(II) and iron(III) are described.

The arylazooximes (I) are obtained<sup>1,2</sup> by nitrosation of arylhydrazones of aldehydes with n-butylnitrite:

Previous work from this laboratory<sup>2,3</sup> has shown that the arylazooximes are extensively hydrogen bonded and exhibit <u>cis-trans</u> isomerism (around C=N) in solution. In what follows the ligand (I) will be abbreviated as Haao and its conjugate base  $[R-C(=NO)+N=NAr]^{-}$  as aao.

Many years ago Fiegl<sup>4</sup> studied the "salt formation" ability of phenylazoacetaldoxime with copper(II). Hunter and Roberts<sup>5</sup> first observed that arylazooximes undergo a fast reaction with cobalt(II) acetate in alcohol producing purple tris complexes of trivalent cobalt Co(aao)<sub>3</sub>. They suggested without any substantial evidence a six membered chelate ring (II). Malatesta and Pizzoti<sup>6</sup> described the diamagnetic bis complexes of nickel(II) which they formulated as (III) with five membered chelate rings. The infrared, electronic and pmr spectra of Co(aao)<sub>3</sub><sup>7</sup> and Rh(aao)<sub>3</sub><sup>8</sup> were studied in this laboratory some time ago. The chelate rings were concluded to be five-membered (IV). The

$$R-C$$
 $N=N$ 
 $R-C$ 
 $N=N$ 
 $N=N$ 

stereochemistry in the cobalt(III) complex is exclusively  $\underline{\text{trans}}$  (V) while the rhodium(III) complexes exist in both  $\underline{\text{cis}}$  (VI) and  $\underline{\text{trans}}$  (V) forms. The observed stereochemistry is related<sup>7,8</sup> to

ligand steric hindrance and metal ion size. Palladium(II) forms halogen bridged complexes (VII) and bis complexes (type III) with arylazooximes. These undergo many bridge splitting and/or chelate ring opening reactions. The dinuclear copper(II) species of the type  $\operatorname{Cu_2(aao)_4}$  are strongly exchange coupled and are diamagnetic. 10

In view of the fact that Haao gives rise to neutral tris complexes  $M(aao)_3$  with cobalt(III) and rhodium(III), it was felt that it will be interesting to obtain the corresponding iron(III) complexes. On the other hand, it is known that ligands having  $\alpha$ -dimmine function (VIII) readily form  $^{11,12}$  deeply coloured-usually cationic-stable complexes of iron(II). Since the arylazooximes contain the  $\alpha$ -azoimine group (IX) which is isoelectronic with VIII, it was thought that arylazooximes may form stable iron(II) complexes, having interesting spectroscopic and other properties (compare with 2-phenylazopyridine (Chapter IV) which also has the function IX).

$$N=C-C=N$$
  $N=C-N=N$  (VIII)

#### V.2 RESULTS AND DISCUSSION

#### A. Synthetic Experiments

In neutral or ammoniacal aqueous solution Haao does not undergo any observable reaction with iron(III) salts such as ferric ammonium sulphate. However, it readily reacts with anhydrous ferric chloride in 95% ethanol. On mixing the reagents, the reaction mixture develops an immediate dark colour. On gentle heating for a few minutes black crystalline solid of composition Fe(aao), 5Cl deposits from the solution. This

compound alone could be isolated even when the Haao: FeCl<sub>3</sub> ratio is made 3:1. Best yields however were obtained when the ratios were 3:2.

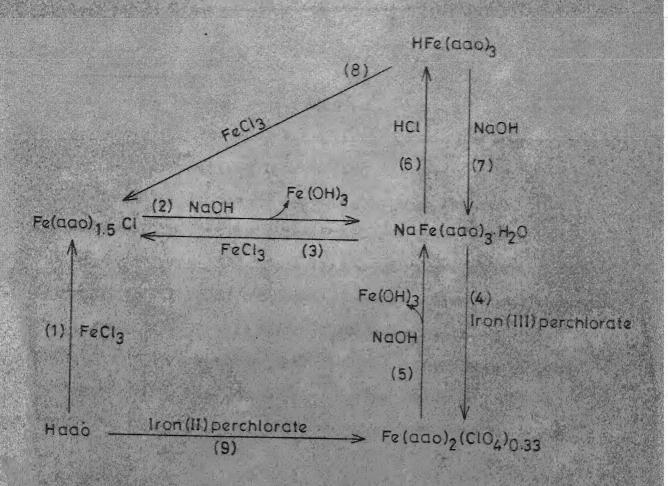
Fe(aao)<sub>1.5</sub>Cl is only sparingly soluble in ethanol, benzene and water. However, it readily dissolves in polar organic solvents such as chloroform, acetone, nitromethane, nitrobenzene etc. giving greenish black solutions. Reaction of an acetone solution with aqueous sodium hydroxide leads to the rejection of Fe(OH)<sub>3</sub> and the formation of a green solution. From this solution NaFe(aao)<sub>3</sub>.H<sub>2</sub>O can be readily isolated in the form of green crystals, which are more or less soluble without any change of colour in a variety of solvents such as benzene, acetone, ethanol, nitromethane, nitrobenzene, water etc. Reaction of NaFe(aao)<sub>3</sub>.H<sub>2</sub>O with anhydrous FeCl<sub>3</sub> in warm 95% ethanol regenerates Fe(aao)<sub>1.5</sub>Cl.

When a solution of NaFe(aao) $_3.H_2$ O in ethanol is treated with dilute HCl, a black crystalline precipitate of composition HFe(aao) $_3$  results. This can be reacted with sodium hydroxide to regenerate NaFe(aao) $_3.H_2$ O. The solubility characteristics of HFe(aao) $_3$  are similar to those of Fe(aao) $_{1.5}$ Cl.

Lastly the reaction of iron(II) perchlorate hexahydrate with Haao, in warm 95% ethanol readily yield black crystals of composition  $\text{Fe(aao)}_2(\text{ClO}_4)_{0.33}$ . Its solubility characteristtics are again similar to those of  $\text{Fe(aao)}_{1.5}^{\text{Cl}}$ .

The reactions described above are summarised in Fig. V.1. The species involved here are then:  $NaFe(aao)_3.H_2O$ ,





### Solvents

(1), (3), (4), (7), (8), (9): 95% Ethanol

(6) : Aqueous ethanol

(2), (5) : Acetone

FIG. V. 1 CHEMICAL INTERCONVERSION OF ARYLAZOOXIMATES

HFe(aao) $_3$ , Fe(aao) $_{1.5}$ Cl and Fe(aao) $_2$ (ClO $_4$ ) $_{0.33}$ . These will now be taken up for discussion.

### B. The System NaFe(aao)<sub>3</sub>.H<sub>2</sub>O

Since each aso has unit negative charge, it is evident that NaFe(aso)<sub>3</sub>.H<sub>2</sub>O contains iron in the oxidation state †2. This is fully corroborated by magnetic and spectral data reported in this section. It will be shown later that Fe(aso)<sub>1.5</sub>Cl (from which NaFe(aso)<sub>3</sub>.H<sub>2</sub>O is obtained) contains from in both the oxidation states +2 and +3. Since this compound is obtained starting from iron(III) chloride, partial reduction must occur during the synthesis. It is well known that FeCl<sub>3</sub> is reduced by alcohol to FeCl<sub>2</sub> under photochemical irradiation.<sup>13</sup> It appears that ethanol can reduce FeCl<sub>3</sub> thermally in the presence of Haso. The mechanism of this reduction was not investigated.

#### a. Magnetic Data

The NaFe(aao) $_3$ . $_{2}^{0}$  system is diamagnetic. After diamagnetic correction, the iron atom is found to be slightly paramagnetic. Two representative examples are shown in Table V.1. The slight paramagnetism of the iron atom is undoubtedly due to temperature independent contributions to susceptibility. The absence of unpaired electrons in this system is corroborated by pmr data, which will be presented later. The low-spin ( $t_{2g}^6$ ) nature of NaFe(aao) $_3$ . $_{2}^{0}$ 0 will be in agreement with a structure,

TABLE V.1

MAGNETIC SUSCEPTIBILITY DATA FOR NaFe(aao)3.H20

Ar=	Compound R=	Temp. OC	xgx10 <sup>6 a</sup>	x <sub>M</sub> x10 <sup>6</sup>	μ <sub>eff</sub> (BM)
С <sub>6</sub> Н <sub>5</sub>	С <sub>6</sub> Н <sub>5</sub>	20.0	-0.39	37	0.29
с <sub>6</sub> н <sub>5</sub>	<u>p</u> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	20.5	-0.38	33	0.28

a.  $\boldsymbol{\chi}_g$  and  $\boldsymbol{\chi}_M$  are gram and corrected molar susceptibilities.

TABLE V.2

INFRARED DATA OF SOME ARYLAZOOXIMES AND NaFe(aao)3.H2O

COMPLEXES IN KBr (DISCS)

			The second secon	
Free ligand R=Ar=C <sub>6</sub> H <sub>5</sub>	NaFe(aao) <sub>3</sub> . $H_2^{O}$ R= Ar= $C_6^{H_5}$	Free ligand $Ar=C_6H_5$ $R = \underline{p}-CH_3-C_6H_4$	NaFe(aao) <sub>3</sub> . $H_2$ O  Ar= $C_6H_5$ R= $\underline{p}$ - $CH_3$ - $C_6H_4$	Assign- ment
3 260	3400	3180	3360	ν <sub>O-H</sub>
1635	1605	1630	1595	$v_{C=N}^{b}$
1038	1280,1242 <sup>d</sup>	1050	1280,1250 <sup>d</sup>	$v_{N-O}^{C}$
690,7 <b>1</b> 5, <b>7</b> 70	690,730,760	690,760,770	700,765	out-of- plane 8 <sub>CH</sub>

 $<sup>^{\</sup>text{a}}\text{broad band;}\quad ^{\text{b}}\text{weak band;}\quad ^{\text{c}}\text{strong band;}\quad ^{\text{d}}\text{either or both could be }\nu_{N-0}$  .

in which iron(II) has a pseudooctahedral  $FeN_6$  coordination sphere. The implication is that the  $Fe(aao)_3^-$  unit may have a structure very similar to that of the isoelectronic  $Co(aao)_3$  species (structure V and VI). However, the iron(II) system has the complication in that binding to  $Na^+$  is to be accounted for. This point will be discussed (vide infra).

#### b. Infrared Data

Vibration spectra of free arylazooximes in the solid state and in solution show an intense and some what broad band (width at half-height  $\sim 50~{\rm cm}^{-1}$ ) in the region 1000-1050 cm $^{-1}$ . This has been assigned to  $v_{\rm N-O}$  of the azooxime moiety. A weak band at  $\sim 1630~{\rm cm}^{-1}$  is due to the C=N stretch. On complex formation (e.g., Co(aao)<sub>3</sub>) the N-O stretch is shifted very considerably to higher frequency due to the contribution of the nitrone structure X. Similar shifts to high frequency occur in NaFe(aao)<sub>3</sub>. H<sub>2</sub>O.

$$\begin{array}{c}
N \longrightarrow N \longrightarrow Ar \\
N \longrightarrow N \longrightarrow 3
\end{array}$$
metal
$$\begin{array}{c}
N \longrightarrow 3
\end{array}$$

$$\begin{array}{c}
N \longrightarrow 3
\end{array}$$

Infact spectra of these complexes are very similar to those of  $\text{Co(aao)}_3$ . Some selected frequency data are set-out in Table V.2. Unlike  $v_{N-O}$ , the C=N stretch is shifted to lower frequencies on complexation. This is expected. The N=N stretch should appear

at  $^{1400}$  cm<sup>-1</sup> (compare Chapter IV). However, arylazooximes show a complex spectrum in this region and we have not been able to identify  $\nu_{\rm N=N}$  with certainty. At the present level of analysis, infrared data alone do not settle the structural question unequivocally. However, indications are strong that a  ${\rm Co(aao)}_3^{-1}$  like species (i.e.,  ${\rm Fe(aao)}_3^{-1}$ ) is present.

### c. Electronic Spectra

In the electronic spectra<sup>2</sup> of free arylazooximes, an  $n-\pi^*$  azo band is clearly seen in the region 455-400 nm ( $\epsilon$ <1000 l.mol<sup>1</sup>cm<sup>1</sup>). The next band is of  $\pi-\pi^*$  origin and is located at  $\sim$ 300 nm. The features in the spectrum of the potassium salt of Haao are found to be essentially similar to those of the parent oxime.

Since the complexes under discussion contain the azoimine fragment (IX), one may expect the presence of metal-ligand charge transfer transitions in the visible region as in the case of 2-phenylazopyridine-iron(II) system,  $\operatorname{Fe}(\operatorname{pap})_3^{2+}$  (Chapter IV). Indeed an intense band at  $^{600}$  nm with an ill-defined shoulder at a slightly higher energy is present in the spectra of NaFe(aao)\_3.  $\operatorname{H}_2^0$  (Table V.3 and Fig. V.2). This band can be assigned to the  $\operatorname{t}_{2g} \to \pi^*$  (azoimine) transition as in the case of  $\operatorname{Fe}(\operatorname{pap})_3^{2+}$ . Interestingly the band positions of  $\operatorname{Fe}(\operatorname{aao})_3^-$  and  $\operatorname{Fe}(\operatorname{pap})_3^{2+}$  are nearly the same. The  $\operatorname{Fe}(\operatorname{aao})_3^-$  system also shows a band at  $^{400}$  nm. A similar band is observable in the Haao complexes of cobalt(III),  $^7$  copper(II) $^{10}$  and palladium(II).  $^{14}$  This band may

TABLE V.3

ABSORPTION MAXIMA ( $\lambda$ , nm) AND EXTINCTION COEFFICIENTS ( $\epsilon$ , L.MOL.  $^{-1}$ , CM  $^{-1}$ ) OF NaFe(aao)  $_3 \cdot \text{H}_2$ O COMPLEXES IN CHLOROFORM SOLUTIONS

Ar =	Compound R=	λ(ε)	
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub> 610(9, 20	610(9,200); 545(6,900)sh; 380(26,000)	380(26,000)
C <sub>6</sub> H <sub>5</sub>	$n^{-C_3}H_7$ 610(9,50	610(9,500); 545(7,100)sh; 380(24,000)	380 (24,000)
$C_6H_5$	C <sub>6</sub> H <sub>5</sub> 610(9,72	610(9,720); 540(7,400)sh; 400(17,600)	400(17,600)
C <sub>6</sub> H <sub>5</sub>	$P^{-CH_3} - C_6H_4$ 610(10,6	610(10,600);540(7,500)sh; 405(15,800)	405 (15,800)

sh: Shoulder.

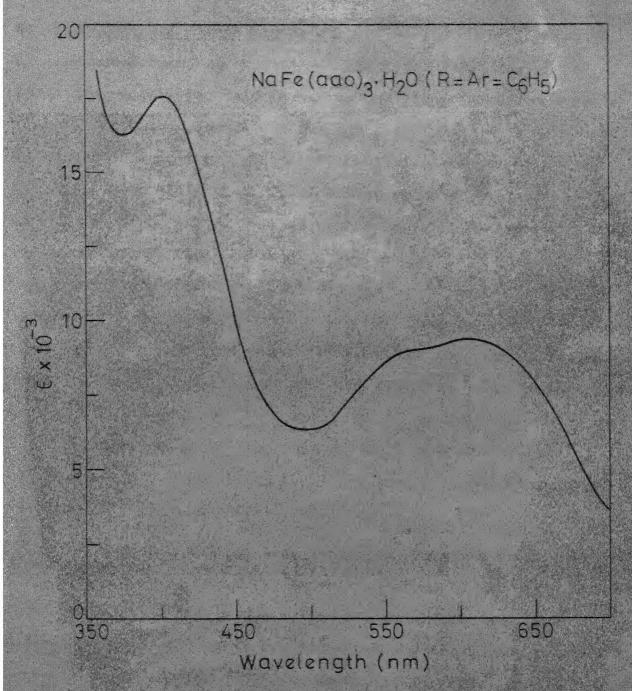


FIG. V. 2 ELECTRONIC SPECTRUM IN CHLOROFORM

represent metal perturbed ligand transitions.

#### d. Proton Magnetic Resonance Spectra

Pseudooctahedral chelates of the type M(AB)<sub>3</sub> can exist in two geometrically isomeric forms <u>cis</u> and <u>trans</u> (AB is an unsymmetrical bidentate ligand). In the <u>cis</u> form, the A ends span facially while in the <u>trans</u> form the distribution is meridional. The <u>cis</u> isomer has a three-fold axis of symmetry whereas the <u>trans</u> isomer has no symmetry. In the <u>cis</u> isomer all chelate rings are therefore in identical environments. On the other hand, in the <u>trans</u> isomer all three chelate rings are in different environments. A given nucleus (or a group of equivalent nuclei) should, in principle have different chemical shifts for the three chelate rings in the <u>trans</u> isomer and the same chemical shift in the <u>cis</u> isomer. This principle has been used 7,8 to establish the stereochemistries of Co(aao)<sub>3</sub> and Rh(aao)<sub>3</sub>. As stated earlier the former complex exists in the <u>trans</u> form (V) while the latter give <u>cis</u> (VI) and <u>trans</u> (V) forms.

We have used the above principle to probe the stereochemistry of the  $Fe(aao)_3$  moiety. In every system studied each substituent gives rise to only <u>one</u> observable signal in  $CDCl_3$  (Table V.4; Fig. V.3). The alkyl region of the spectra of the complex with Ar = phenyl and  $R = \underline{n} - C_3H_7$  is shown in Fig. V.3. Every complex gives rise to a clearly observable water signal (Table V.4). This dissappears on shaking the solution with  $D_2O$ .

TABLE V.4

CHEMICAL SHIFT DATA OF NaFe(aao)3.H2O COMPLEXES

Ar=	ompound R=	Proton type	Chemical shift <sup>a</sup> ppm
С <sub>6</sub> Н <sub>5</sub>	CH <sub>3</sub>	СН <sub>3</sub> Н <sub>2</sub> О	2.20 2.50 <sup>b</sup>
C <sub>6</sub> H <sub>5</sub>	<u>n</u> -C <sub>3</sub> H <sub>7</sub>	СН <sub>3</sub> СН <sub>2</sub> СН <sub>2</sub> СН <sub>3</sub> СН <sub>2</sub> СН <sub>2</sub>	2.91 <sup>c</sup> 1.65 <sup>d</sup> 0.91 <sup>e</sup>
Сн	т-Сн -С н	H <sub>2</sub> O	1.90 <sup>b</sup>
<sup>C</sup> 6 <sup>H</sup> 5	<u>p</u> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	<u>р</u> -с <u>н</u> <sub>3</sub> -с <sub>6</sub> н <sub>4</sub>	2.20 <sup>b</sup>

a. Chemical shifts are from tetramethylsilane measured at 100 MHz in  $\mathrm{CDCl}_3$ .

b. Broad signal, vanishes on shaking the solution with a drop of  $\mathrm{D}_2\mathrm{O}$ .

c. Centre of a broad signal (triplet) with half height 20 Hz.

d. Centre of a sextet (J = 7 Hz).

e. Centre of a triplet (J = 7 Hz).

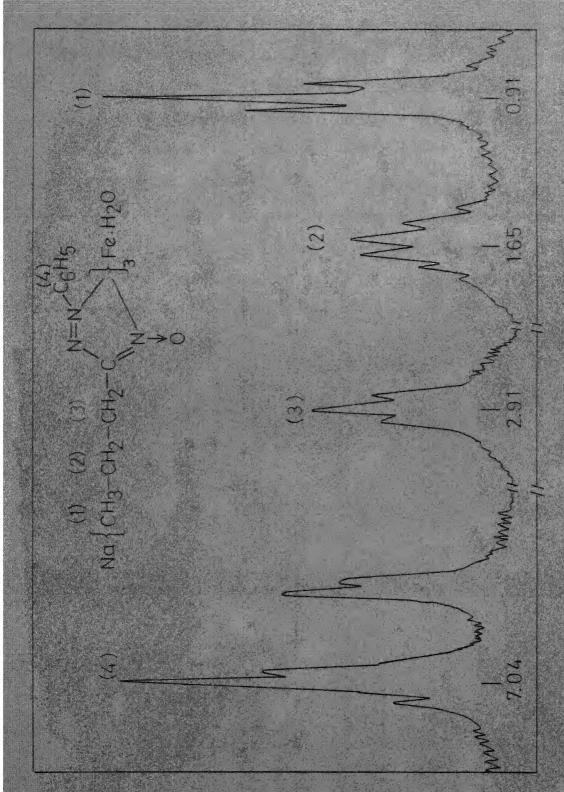


FIG Y. 3 PMR SPECTRUM OF NaFe(ado) 3. H2O (R-1-C3H7; Ar = C6H5) IN CDC13. CHEMICAL SHIFTS ARE FROM TETRAMETHYLSILANE IN PPM

The pmr spectra of NaFe(aao)<sub>3</sub>.H<sub>2</sub>O strongly suggest a <u>cis</u> structure (VI) for the Fe(aao)<sub>3</sub> moiety (a nonrigid <u>trans</u> structure is of course not eliminated). In this connection it may be significant that the preference of iron(II) for the <u>cis</u> stereochemistry in anionic tris chelates of bidentate oxime ligands is well documented in several cases. Mention may be made of ferroverdin<sup>16</sup> (XI), a green naturally occurring quinone-oxime tris complex of iron(II) and iron(II) violuret complex<sup>17</sup> (XII). In each of these cases solvated salts of the type NaFeL<sub>3</sub> are readily isolated in the solid state.

$$H_2C = CH - \bigcirc O - C - \bigcirc O$$

Fe Na<sup>+</sup>. Solvent

(XII)

### e. Solution Electrical Conductivity Data: Binding of Sodium Ion

The fact that NaFe(aao)<sub>3</sub>H<sub>2</sub>O is soluble in nonpolar solvents like benzene (<u>infact the solubility in benzene is considerably more than that in water</u>) strongly suggests that the sodium ion is chemically bound to the Fe(aao)<sub>3</sub> moiety. This is corroborated by the observation that solutions of NaFe(aao)<sub>3</sub>.H<sub>2</sub>O in nitromethane or nitrobenzene have low conductivities at room temperature (Table V.5). The expected conductivities for 1:1 electrolytes in nitromethane and nitrobenzene respectively lie<sup>18</sup> in the ranges 75-95 and 20-30 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>. The observed conductivities clearly show that ion separation occurs only to a very limited extent in solutions of NaFe(aao)<sub>3</sub>.H<sub>2</sub>O in nitrohydrocarbons. The sodium ion evidently remains largely bound in a complexed form.

On the basis of these data alone it is not possible to make any specific suggestions about the stereochemistry and the mode of bonding of sodium. However, it is very likely that the oxygen atoms of the oxime functions and of the solvent of crystallisation are involved in coordination with sodium ion. This is schematically represented in structure XIII. Coordination of

TABLE V.5

CONDUCTIVITY DATA FOR NaFe(aao) $_3$ .H $_2$ O COMPLEXES AT  $_2$ S $_2$ C

		SOLVenc	concentration mol. lit.1	ohm $^{-1}$ , cm $^2$ mo $^{1}$
C6H5 D-C3H7	3 H <sub>7</sub>	Nitrobenzene	1.8x10 <sup>-3</sup>	0.2
C6H5 P-C	P-CH3-C6H4	Nitrobenzene	3.7x10 <sup>-3</sup>	0.3
C <sub>6</sub> H <sub>5</sub>	P-CH3-C6H4	Nitromethane	1.5x10 <sup>-3</sup>	21.0

oxime oxygen to sodium ion is known to occur in the triclinic form of ferroverdin<sup>16</sup> (XI). It is also noted that in 2:1 adducts of picolinic-N-oxide with sodium iodide, the sodium ions<sup>19</sup> are believed to be coordinated to the N-oxide oxygen. A related information is that in the potassium salt of isonitrosoaceto-phenone, the binding of potassium ion to oxime oxygen occurs.<sup>20</sup> It will be appropriate to call NaFe(aao)<sub>3</sub>.H<sub>2</sub>O as a mixed complex in which the arylazooxime moiety binds both iron(II) and sodium(I).

## C. System HFe(aao)<sub>3</sub>

This is obtained by the following reaction which

$$NaFe(aao)_3.H_2O + HCl \xrightarrow{ethanol} HFe(aao)_3 + NaCl$$
 (2)

was only briefly investigated. The solids are diamagnetic and have low electrical conductivity (Table V.6) in nitromethane solution. Their ir (Table V.6) and electronic spectra (Table V.6, and Fig. V.4) are closely akin to those of NaFe(aao) $_3$ .  $H_2O$ . Evidently HFe(aao) $_3$  contains a proton bound to Fe(aao) $_3$ . The most probable binding site is oxime oxygen. Whether the proton is bound to one oxygen or is chelated to more than one oxygen atom: (intramolecularly or intermolecularly) is not certain. No clearly observable  $\nu_{\rm OH}$  frequency could be located in the region 2000-3500 cm $^{-1}$ . However, a broad band of moderate intensity at  $\sim 1680$  cm $^{-1}$  is present in these systems. Strongly chelated O--H--O

## TABLE V.6

ELECTRICAL CONDUCTIVITY, INFRARED FREQUENCIES (Cm $^{-1}$ ), ABSORPTION MAXIMA ( $\lambda$ , nm) AND EXTINCTION COEFFICIENTS ( $\epsilon$ , L.MOL $^{-1}$ .CM $^{-1}$ ) OF HFe(aao) $_3$  COMPLEXES

Cond	uctivity Data (Nitron	nethane)	
	Compound	Concentration (mol.lit <sup>-1</sup> )	$(ohm^{-1}.cm^2.mol^{-1})$
	$R=Ar=C_6H_5$	$1.04 \times 10^{-3}$	3
	Ar=C <sub>6</sub> H <sub>5</sub> ;	$9.67 \times 10^{-4}$	4
0	R = p-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	ين بيند ويون ويون ويون ميند ميند ميند ميند ميند اليام مين ويون ويون ويون ويون ويون ويون ويون	
Infr	ared Data <sup>a</sup>		
	$R = Ar = C_6 H_5$	HFe(aao) <sub>3</sub> Ar=C <sub>6</sub> H <sub>5</sub> R=p-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	Assignment
	3400	3400	v О-Н
	1603	1610	$v^{C=N}$
	1270,1240	1270,1240	v <sub>N-O</sub>
_	738,765,688	630,760,690	Out-of-plane $\delta_{ ext{CH}}$
Elect	ronic Spectral Datab		
	Compound	λ(ε)	
	R=Ar=C6H5	560(10,131); 413(1	5,743)
	$Ar=C_6H_5;$ $R=p-CH_3-C_6H_4$	570(11,676); 420(1	6,523)

a. Infrared spectra were run in KBr discs.

b. Electronic spectra were run in chloroform solutions.

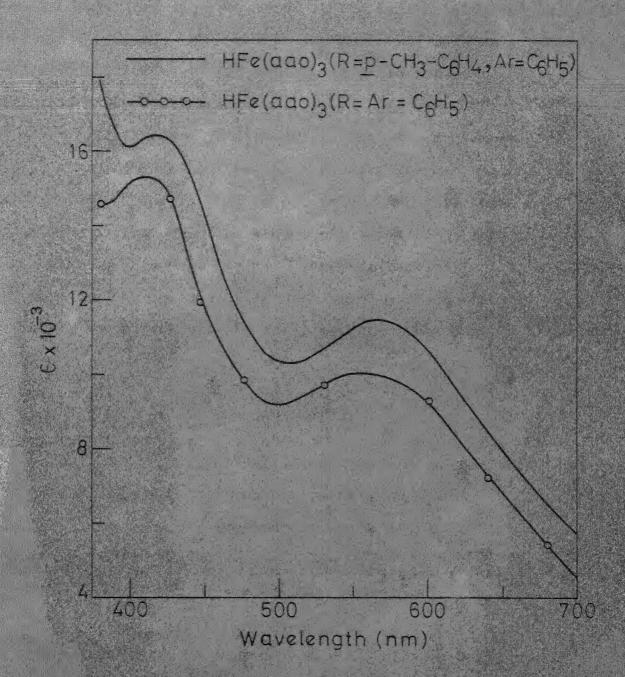


FIG V.4 ELECTRONIC SPECTRA IN CHLOROFORM

groups (as present in bis-dimethylglyoximato complexes) are known to show bending vibrations in the region  $1600-1800 \text{ cm}^{-1}$ , and the stretching vibration at  $2200-2400 \text{ cm}^{-1}$  are observed with difficulty. By analogy it would appear that  $\text{HFe}(\text{aao})_3$  has a strongly chelated proton. In the <u>cis</u> stereochemistry of  $\text{Fe}(\text{aao})_3^-$  (VI) the possibility exists that the proton is simultaneously bonded to all the three oximato oxygen atoms of the same  $\text{Fe}(\text{aao})_3^-$  unit. This is not to say that all three O--H bonds are equivalent. The proton may actually be held in a potential well with several minima. However, this may not at all represent the true nature of the chelation present which may very well be intermolecular. We shall not speculate on this issue any further.

# D. System Fe(aao)<sub>1.5</sub>Cl

This is the initial product of reaction of Haao with FeCl<sub>3</sub> in ethanol (Fig.V.1). On reaction with aqueous sodium hydroxide the following quantitative reaction occurs:

$$2Fe(aao)_{1.5}Cl + 3NaOH \xrightarrow{H_2O} Fe(OH)_3 + NaFe(aao)_3.H_2O + 2NaCl$$
 (3)

One mole of  $\text{Fe(OH)}_3$  is rejected per two moles of  $\text{Fe(aao)}_{1.5}^{\text{Cl.}}$ Since  $\text{NaFe(aao)}_3.\text{H}_2^{\text{O}}$  is formed so readily, it would appear that  $\text{Fe(aao)}_{1.5}^{\text{Cl}}$  has at least half of the iron in bivalent state. Rejection of  $\text{Fe(OH)}_3$  under alkali attack does not prove the initial presence of iron(III), since aerial oxidation may occur under the reaction conditions. However, careful experiments under oxygen free nitrogen atmosphere also led to the generation of  $\text{Fe(OH)}_3$ . It does appear that some of the iron in  $\text{Fe(aao)}_{1.5}^{\text{Cl}}$  is present in the oxidation state +3. The reconstitution of  $\text{Fe(aao)}_{1.5}^{\text{Cl}}$  from  $\text{NaFe(aao)}_3.\text{H}_2\text{O}$  by the reaction (4) provides

$$NaFe(aao)_3 \cdot H_2O + FeCl_3 \xrightarrow{ethanol} 2Fe(aao)_{1.5}Cl + NaCl + H_2O$$
 (4)

further evidence in favour of the postulated presence of both iron(II) and iron(III) in the probable ratio 1:1. It would also appear that iron(II) is present in the form of the tris chelate  $Fe(aao)_3^-$ .

#### a. Bulk Magnetic Susceptibility Data

The Fe(aao)<sub>1.5</sub>Cl systems are strongly paramagnetic showing the presence of iron in the high-spin configuration. Unlike NaFe(aao)<sub>3</sub>.H<sub>2</sub>O, this system gives ill defined pmr spectra with very broad lines showing the presence of fast relaxation characteristic of paramagnetic systems. The bulk susceptibility of several Fe(aao)<sub>1.5</sub>Cl species were measured both in the solid state and in chloroform solution. Data are presented in Table V.7. The magnetic moment is found to be ~4.2 BM per iron atom. However, assuming a doubled formula weight i.e., [Fe(aao)<sub>1.5</sub>Cl]<sub>2</sub> and assuming that one iron atom is present in the low-spin +2

TABLE V,7

MAGNETIC SUSCEPTIBILITY DATA OF Fe(aao) $_{1,5}$ Cl COMPLEXES IN SOLID STATE AND IN CHLOROFORM SOLUTION

Com	Compound	Temp.	\$ 410	8 9 × ×	B (1/4)	q 9°; ^	
Ar=	K II	၀	day	FALO	heff'BM)	OIX.W	h'eff(BM)~
SOLID STATE	STATE		*				And the state of t
$c_{6}$ $H_{5}$	n-C3 H7	28.5	18.74	7175	4.17	14350	5,90
$^{\mathrm{C}_{6}\mathrm{H}_{5}}$	C6 H5	27	17.17	7475	4.25	14950	6.01
$C_6H_5$	р-СН <sub>3</sub> С <sub>6</sub> Н <sub>4</sub>	28	15.86	7309	4.21	14619	т Ф С
CHLORO	CHLOROFORM SOLUTION				1 1	) † † •	0 • • •
C <sub>6</sub> H <sub>5</sub>	n-C3H7	<b>58</b>	18,95	7255	4.19	14510	5.93
$c_6 H_5$	C <sub>H</sub> <sub>5</sub>	59	16.76	7294	4.21	14589	5.96
C <sub>6</sub> H <sub>5</sub>	P-CH3 C6 H4	28.5	15.49	7455	4.25	14190	5 . 87
SPECIAL SPECIA							

is the corrected susceptibility calculated using the formula Fe(aao) $_{1\,\,\,\,5}\,\mathrm{cl}$ and  $\mu$  is the magnetic moment based on this. о О

 $b_{ullet}$  µ'is computed using the formula weight Fe $_2$ (aao) $_3$ Cl $_2$  and assuming that only one iron atom is paramagnetic and relationship between  $\mu$  and  $\mu^{\prime}$  is  $\mu = \frac{1}{\sqrt{2}} - \mu^{\prime}$  oxidation state, the magnetic moment of the other iron atom (Table V.7) turns out to be ~5.9 BM. This value is in line with a high-spin d<sup>5</sup> configuration. The magnetic data are thus consistent with the presence of low-spin iron(II) and high-spin iron(III) in the molar ratio 1:1 in Fe(aao)<sub>1.5</sub>Cl.

## b. Clue to Molecular Nature: The Case of Fe(aao)2(ClO4)0.33

The first clue to the actual nature of  $\mathrm{Fe(aao)}_{1.5}^{\mathrm{Cl}}$  was obtained while investigating the species  $\mathrm{Fe(aao)}_{2}^{\mathrm{ClO}_{4}^{\mathrm{O}}_{0.33}^{\mathrm{Cl}}}$ . This species was initially obtained by a direct reaction between iron(II) perchlorate and Haao. We were hoping to obtain tetragonal systems of the type  $\mathrm{Fe(aao)}_{(\mathrm{Haao})}(\mathrm{ClO}_{4}^{\mathrm{O}})$ . Such a system was never obtained. The odd species  $\mathrm{Fe(aao)}_{2}^{\mathrm{ClO}_{4}^{\mathrm{O}}_{0.33}^{\mathrm{O}}}$  resulted instead. In course of synthesis at least part of the iron has got oxidised to the +3 state. We later observed that the same species could be obtained by reacting iron(III) perchlorate (1 mol) with NaFe(aao)\_3.H\_2O (2 mol) (Fig. V.1). This synthetic reaction is:

$$2NaFe(aao)_3.H_2O + Fe(ClO_4)_3 \longrightarrow$$

$$3Fe(aao)_2(ClO_4)_{0.33}^+ 2NaClO_4$$
 (5)

On the other hand the perchlorate quantitatively looses 1/3 of its iron content as  $Fe(OH)_3$  and is converted to  $NaFe(aao)_3.H_2O$ , on reaction with sodium hydroxide according to the reaction:

$$3Fe(aao)_{2}(ClO_{4})_{0.33} + 3NaOH \xrightarrow{H_{2}O}$$

$$Fe(OH)_{3} + 2NaFe(aao)_{3} \cdot H_{2}O + NaClO_{4}$$
 (6)

The above observations led us to suspect that  $Fe(aao)_2^{(ClO_4)}_{O.33}$  may contain iron(III) bound in some way to  $Fe(aao)_3^-$  with perchlorate balancing the extra positive charge as in

The weight of this formula is equal to that of  $3\text{Fe}(aao)_2(\text{ClO}_4)_{0.33}$ . It is readily seen that with the above formulation the reaction (5) and (6) can be rationalised as:

$$2Fe(aao)_{3}^{-} \xrightarrow{+Fe^{3+}} [Fe(Fe(aao)_{3})_{2}]^{+}$$

$$(-Fe(OH)_{3})$$

$$(7)$$

The electrical conductivity (calculated on formula  $[Fe(Fe(aao)_3)_2]Clo_4$ ) in nitromethane solution (20°C) is in excellent agreement with 1:1 electrolytic behaviour (Table V.8). The powder magnetic susceptibility of one system viz.,  $R=Ar=C_6H_5$  was determined (Table V.8). The results show that system contains five unpaired electrons. This is readily understandable if one assumes that the iron(II) atoms are low-spin (a fully justified assumption in view of the results on NaFe(aao)<sub>3</sub>. $H_2$ 0) while the iron(III) atom is high-spin.

TABLE V.8

ELECTRICAL CONDUCTIVITY AND MAGNETIC DATA OF [Fe(Fe(aao) $_3$ ) $_2$ ]ClO $_4$ 

\(\left(\text{ohm}^{-1}\cm^2\cdotmo1^{-1}\right)\)		igs unit) $\mu_{\rm eff}({\rm BM})$	.67 5.80	
Concentration (mol.lit. <sup>-1</sup> ) 7.345 x 10 <sup>-4</sup> 3.585 x 10 <sup>-4</sup>		$x_M \times 10^6$ (cgs unit)	14167	
Data (Nitromethane)  Compound $R = Ar = C_6H_5$ $Ar = C_6H_5$ $R = P - CH_3 - C_6H_4$	E	$\chi_{\rm g} \propto 10^6 ({\rm cgs~unit})$	8.3	
Conductivity Data Complex R= Ar Ar= Ce R= P-(		Temp.	21.5	

With these informations at hand, a reexamination of the properties of  $Fe(aao)_{1.5}^{Cl}$  described earlier (and spectral properties to be described later) led us to examine the formulation:

which has the same formula weight as  $4\text{Fe(aao)}_{1.5}\text{Cl.}$  The difference between the 'perchlorate' and the 'chloride' lies in the replacement of  $\text{ClO}_4^-$  by  $\text{FeCl}_4^-$  in the anionic part. Both have the same trinuclear cation. The magnetic data of Table V.8 are in full agreement with such a formulation. Of the four iron atoms two (both iron(II) are present in the cation) are lowspin and two (both are iron(III); one is present in the cation and one in the anion) are high-spin (d<sup>5</sup>). Only half of the iron atoms thus contribute to paramagnetic susceptibility. The reactions (2) and (3) can then be rationalised

The electrical conductivity data are in full agreement with the above formula (Table V.9). The  $[Fe(Fe(aao)_3)_2]FeCl_4$  system is a well behaved 1:1 electrolyte. <sup>18</sup>

TABLE V.9

ELECTRICAL CONDUCTIVITY OF [Fe(Fe(aao) $_3$ ) $_2$ ]FeCl $_4$  COMPLEXES AT  $_2$ CO

Compound	Solvent	Concentration	A 1 - 1,
	t and the section of	/ MO1.11C /	( TOW . MO. MILO)
CeH5 CeH5	Nitromethane	$1.88 \times 10^{-3}$	76
$c_6 H_5$ $p^{-CH_3} - c_6 H_4$	Nitromethane	$1.47 \times 10^{-3}$	76
C6 H5 P-CH3-C6 H4	Nitrobenzene	3.37 × 10 <sup>-3</sup>	18
на Мария (перед на доставления в перед пред пред пред пред пред пред пре			

## c. Infrared Data

In the region 4000-600 cm<sup>-1</sup> the infrared spectra of  $[\text{Fe}(\text{Fe}(\text{aao})_3)_2] \times (\text{X} = \text{ClO}_4, \text{FeCl}_4)$  are closely akin to that of  $\text{NaFe}(\text{aao})_3.\text{H}_2\text{O}$  except for small differences in frequencies and the relative intensities of bands. (Of course the  $\nu_{\text{OH}}$  band is absent in the former system, which has additional perchlorate bands for the case  $\text{X} = \text{ClO}_4$ ). This corroborates the presence of bound  $\text{Fe}(\text{aao})_3^-$  moiety in both systems.

Among the  $[Fe(Fe(aao)_3)_2]X$  species, the spectrum (region 4000-600 cm<sup>-1</sup>), of  $X = Clo_4$  is virtually superposable on the spectrum of  $X = FeCl_4$  except for the  $Clo_4$  absorptions which appear only in the former complex. A representative example is shown in the Fig. V.5. Selected frequencies are set out in Table V.10.

Of the four perchlorate vibrations only  $v_3$  and  $v_4$  are ir active. <sup>23</sup> [Fe(Fe(aao)<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> shows  $v_3$  and  $v_4$  bands at ~1085 and ~630 cm<sup>-1</sup> respectively (Fig. V.5 & Table V.10). The  $v_3$  band shows no sign of splitting and the observed spectra are in full agreement with the presence of ionic  $ClO_4$  in the crystal lattice.

The spectra in the low frequency region (500-300 cm<sup>-1</sup>) are displayed in the Fig. V.6 for NaFe(aao)<sub>3</sub>.H<sub>2</sub>O and [Fe(Fe(aao)<sub>3</sub>)<sub>2</sub>]X (X=ClO<sub>4</sub>, FeCl<sub>4</sub>) where the ligand has R=Ar=C<sub>6</sub>H<sub>5</sub> or R=p-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub> and Ar=C<sub>6</sub>H<sub>5</sub>. The following observations are in order:

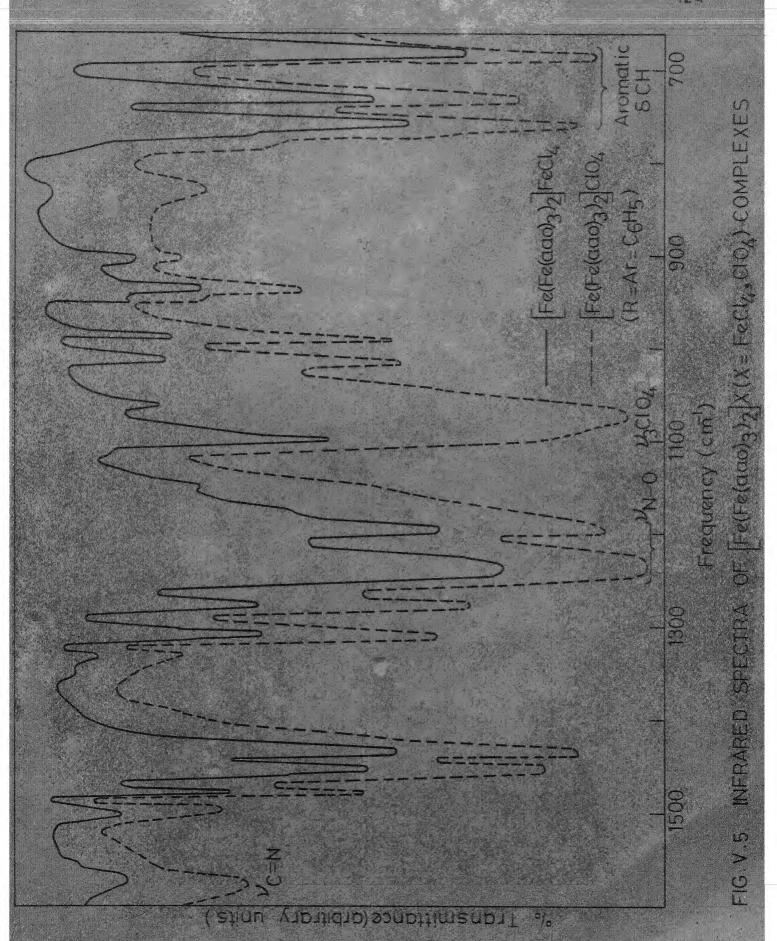
(1) NaFe(aao) $_3 \cdot H_2^0$  does <u>not</u> show any major bands in this region (the same is true of the free ligands whose ir spectra

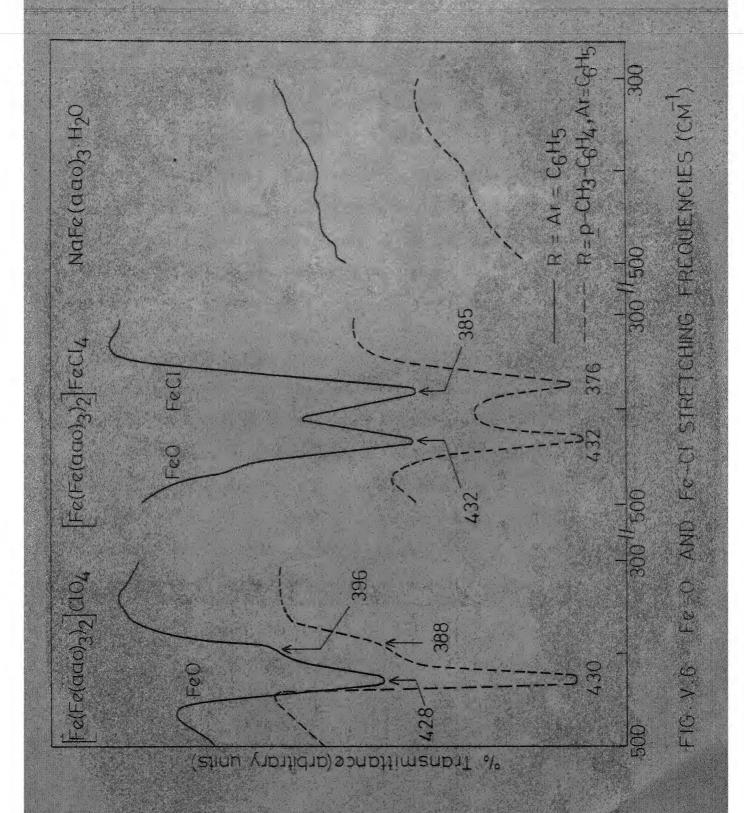
TABLE V.10

SELECTED INFRARED STRETCHING FREQUENCIES<sup>a, b</sup> ( $cm^{-1}$ )

-					Control of the Party of the Par
F.	Fe(Fe(aao) <sub>3</sub> ) <sub>2</sub> ]FeCl <sub>4</sub> $R = Ar = C_6H_5$	[Fe(Fe(aao) <sub>3</sub> ) <sub>2</sub> ]FeCl <sub>4</sub> [Fe(Fe(aao) <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> Ar=C <sub>6</sub> H <sub>5</sub> ; R= $\underline{P}$ -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	$[Fe(Fe(aao)_3)_2]Clo_4$ $R=Ar=C_6H_5$	[Fe(Fe(aao) <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> Ar=C <sub>6</sub> H <sub>5</sub> ; R= $\underline{p}$ -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	Assignment
	1585	1605	1685	1605	V C=N
	1240,1202	1245,1205	1240,1200	1245,1205	N-0
	i i	*.	1085	1085	v3C104
	ľ		630	635	v4C104
	762,737,690	830,760,690	770,760,690	830,760,690	Out-of- plane $\delta_{\mathrm{CH}}$
•	432	432	428	430	VFe(III)-0
	385	376	•	ť	v <sub>3</sub> Fe-Cl
			1.		The state of the s

were run in KBr discs. spectra were taken in nujol mull. a. All the spectra in the region 4000-600 cm b. Below 600 cm spectra were taken in nujol





were also run). Any Fe(II)-N and Na-O frequency present in this region is too weak to be observed.

- (2)  $[\text{Fe(Fe(aao)}_3)_2]\text{FeCl}_4$  shows a strong band at 385 cm<sup>-1</sup>. This band which is absent in the corresponding perchlorate is assigned<sup>24</sup> to  $v_3$  (essentially Fe-Cl stretch) of FeCl<sub>4</sub>.
- (3)  $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{ClO}_4$  exhibits a band at  $\sqrt{430}$  cm<sup>-1</sup> with a shoulder at  $\sqrt{390}$  cm<sup>-1</sup>. A corresponding band is also observed in  $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]\text{FeCl}_4$  at 432 cm<sup>-1</sup>. We believe that this is due to the Fe(III)-O stretch arising out of the bonding of Fe(III) to oxime oxygen atoms. This point is considered below:

#### d. Binding of Iron(III)

In view of the results described so far, it is reasonable to propose that in the mixed valence species the  $Fe(aao)_3$  moiety has the same gross structure as in  $NaFe(aao)_3 \cdot H_2O$ . Since  $[Fe(Fe(aao)_3)_2]^{\dagger}$  behaves as a single cation (conductivity data), the iron(III) atom is evidently bound to the  $Fe(aao)_3$  units. The most reasonable mode of bonding could be one in which iron-(III) is attached to the oxygen atoms of the oxime groups shown

in structure XIV. In XIV, the oxime function is acting as a bridging group between Fe(II) and Fe(III). This is one instance (a very unusual one) of the more general case  $^{25,26}$  (XV). This structural type (XV) has been established for M=M'=Cu, Ni, Pd; M=Cu, M'=Ni etc.

In XIV, the bonding to Fe(III) is essentially the bonding of a N-oxide oxygen (sp<sup>2</sup>N). Pseudooctahedral iron(III) complexes of neutral monodentate or bidentate N-oxides are well known e.g.,  $[Fe(pyo)_6](ClO_4)_3$  (ref. 29),  $[Fe(bipyo_2)_3](ClO_4)_3$ . 3H<sub>2</sub>O (ref. 3O), and  $[Fe(pheno)_3](NO_3)_2$  (ref. 31). In the former

two species the coordination sphere is high-spin  $\text{FeO}_6$ . In the third species the  $\text{FeO}_3\text{N}_3$  coordination sphere shows low-spin — high-spin equilibrium. In strictly octahedral  $\text{MO}_6$  only one degenerate ir active M-O stretch is expected. When the symmetry is lower, two M-O bands are often observed  $^{23}$  (removal of degeneracy). The N-oxide complexes of iron(III) (FeO<sub>6</sub> coordination sphere) show one or two ir bands assignable to Fe-O, e.g.,

$$[Fe(pyo)_{6}](Clo_{4})_{3}$$
 383 cm<sup>-1</sup>(strong) (ref. 29)

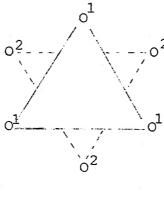
In  $[Fe(Fe(aao)_3)_2]X$ , the band at ~430 cm<sup>-1</sup> (together with the shoulder at ~390 cm<sup>-1</sup>)(Fig. V.6) is assigned to Fe(III)-O stretch. The oxime oxygen of negatively charged  $Fe(aao)_3$  moiety binds to iron(III) more strongly than do the neutral N-oxide ligands.

It is possible to suggest a probable stereochemistry for the iron(III) atom on the basis of general considerations, model building and experimental results.

In molecular systems iron(III) in combination with oxygen ligands usually exhibits grossly octahedral geometry. The FeO<sub>6</sub> coordination sphere is <u>always</u> high-spin (tetrahedral Fe(III)-O<sub>4</sub> is known to exist quite commonly in oxide lattices e.g., in orthoclase feldspar (KAlSi<sub>3</sub>O<sub>8</sub>) containing a small percentage of Fe<sup>3+</sup> in place of Al<sup>3+</sup> (ref. 32)).

In  $[Fe(Fe(aao)_3)_2]^{\dagger}$ , an octahedral stereochemistry on iron-(III) can be readily achieved from <u>cis</u> stereochemistry (structure VI) of  $Fe(aao)_3^{\dagger}$  (compare with the case of NaFe(aao)\_3.H\_2O). In this geometry, the three oxime functions span the same face of the iron(II) octahedron (VI). The lone pairs on the three oxime oxygen atoms (roughly sp<sup>3</sup> hybridised) are correctly directed to bind to the three corners of a face of the iron(III) octahedron.

A second <u>cis</u>  $Fe(aao)_3^-$  unit can then similarly bind to another face completing the iron(III) octahedron. This is schematically shown in (XIX), in which the oxygen atoms coming from the same  $Fe(aao)_3^-$  unit carry the same number on the top. A clearer view of this structure can be obtained from the drawing in Fig. V.7.



(XIX)

The Fe(II)-Fe(III)-Fe(II) chain is essentially linear (lying on an idealised three-fold axis) in this structure.

The observed high-spin character of iron(III) is consistent with this structure (FeO $_6$  coordination sphere). In such a structure the strict symmetry of FeO $_6$  can in no case be  $\mathrm{O}_{\mathrm{h}}$ . The actual symmetry may be quite low depending on the distortions present. In this context it is significant that two Fe-O stretches (band at  $\sim 430~\mathrm{cm}^{-1}$  and shoulder at  $\sim 390~\mathrm{cm}^{-1}$ ) are observed (Fig. V.6).

#### f. Electronic Spectra

The electronic spectra of several  $[Fe(Fe(aao)_3)_2]X$  (X=FeCl<sub>4</sub>, ClO<sub>4</sub>) species were run in chloroform solution. Data are presented

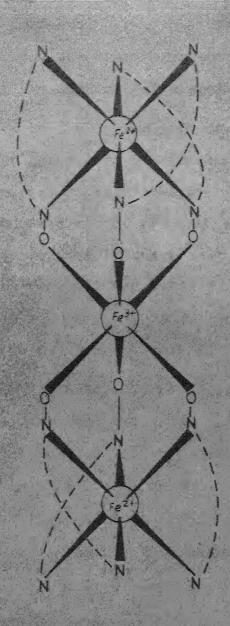


FIG. V 7 BINDING OF IRON(III) IN [Fe(Fe(aao)3)2] X
(X = ClO4, FeCl4)

in Table V.11 and Fig. V.8. No other bands are observed above 600 nm. Two characteristic bands are seen at  $^{\circ}600$  nm and  $^{\circ}470$  nm. Both bands correspond to allowed transitions. For a given R and Ar group, the spectrum is independent of X, showing that both transitions are due to  $[Fe(Fe(aao)_3)_2]^{\dagger}$ .

It is reasonable to assign the ~600 nm band to the metal > ligand charge transfer transition within the Fe(aao) unit (compare with NaFe(aao) .H<sub>2</sub>O: Section V.B). It is significant that the extinction coefficient of the ~600 nm band in [Fe(Fe(aao) )2]X is approximately twice that of NaFe(aao) .H<sub>2</sub>O (compare Fig. V.8 with Fig. V.2 and Table V.11 with Table V.3). This is expected since each mole of [Fe(Fe(aao) )2]X and NaFe(aao) .H<sub>2</sub>O contains two and one mole of Fe(aao) respectively.

The origin of the band at  $^470$  nm is less certain. However, it appears that it has the same origin as the  $^4400$  nm band of  ${
m NaFe(aao)}_3.{
m H}_2{
m O}$ . This band is quite sensitive to the cation to which  ${
m Fe(aao)}_3^-$  is bound. For example when the cation is H (Section C), this band is at  $^420$  nm. This shifts to  $^4440$  nm, when the cation  ${
m Ni}^{2+}$  (see below). Thus there is a systematic shift to lower energy in the order  ${
m Na}^+>{
m H}^+>{
m Ni}^{2+}>{
m Fe}^{3+}$ .

High-spin iron(III) can exhibit only spin-forbidden ligand field transitions. Grossly octahedral  ${\rm FeO}_6$  moiety is known to show  $^{3\,2}$  several such transitions of very low intensity in the range 790-360 nm.  $[{\rm Fe(Fe(aao)}_3)_2]{\rm X}$  may be expected to show similar transitions. When  ${\rm X=FeCl}_4$ , additional spin-forbidden transitions

TABLE V.11

ABSORPTION MAXIMA (A, nm) AND EXTINCTION COEFFICIENTS (  $\epsilon$ , L.MOL $^{-1}$ , CM $^{-1}$ ) OF [Fe(Fe(aao) $_3$ ) $_2$ ]X (X = FeC1 $_4$ , ClO $_4$ ) COMPLEXES IN CHLOROFORM SOLUTIONS

	600(22,754); 460(37,724); 355(49,400)sh 600(23,400); 480(34,900); 355(51,866)sh.	
λ(ε)	460(37,724);	460(44,000).
	600(22,754);	595(26,193); 460(44,000)
Compound	[Fe(Fe(aao) <sub>3</sub> ) <sub>2</sub> ]FeCl <sub>4</sub> $R = Ar = C_6 H_5$ $Ar = C_6 H_5;$ $R = P - CH_3 - C_6 H_4$	[Fe(Fe(aao) <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> $R = Ar = C_6 H_5$

sh, Shoulder,

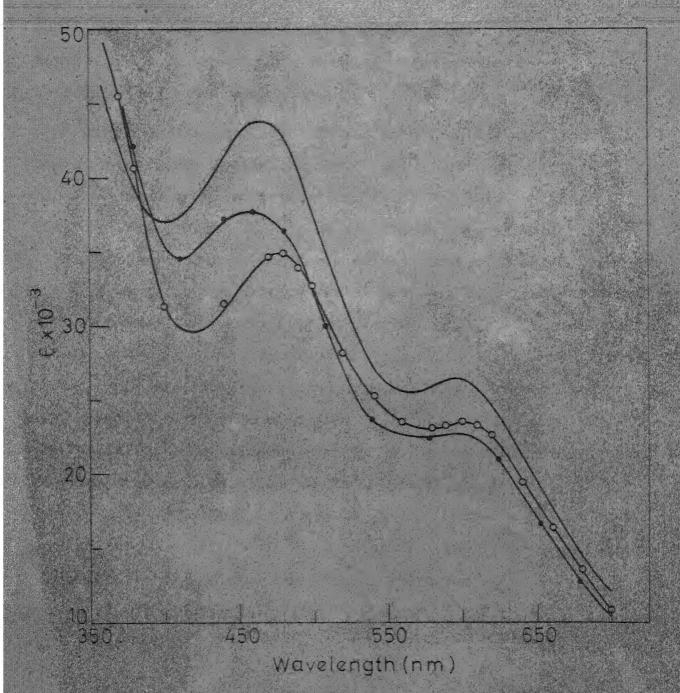


FIG. V.8 ELECTRONIC SPECTRA OF  $[Fe(Fe(aao)_3)_2] CIO_4$   $(R=Ar=C_6H_5)(---), [Fe(Fe(aao)_3)_2] FeCI_4$   $(R=p-CH_3-C_6H_4; Ar=C_6H_5)(---) AND [Fe(Fe(aao)_3)_2]$   $FeCI_4 (R=Ar=C_6H_5)(----) IN CHLOROFORM$ 

due to FeCl<sub>4</sub> are also expected. However, the existence of intense bands in the visible region precludes experimental observations of all such transitions.

Since [Fe(Fe(aao)3)2]X contain both iron(II) and iron(III) linked by a bridge system one may expect a low-energy intervalence charge transfer transition: Fe(II) → Fe(III) (Class II mixed valence system). 33-36 The absorption intensity of this transition depends upon the small delocalisation of the optical electron over the two valence states. When the two valence sites are well-separated (as is true in  $[Fe(Fe(aao)_3)_2]X$ ), the delocalisation occurs via higher order perturbation involving  $M \rightarrow ligand$ , ligand -> M' electron transfer configurations. An ideal example of a class II mixed valence system is Prussian blue which like  $[Fe(Fe(aao)_3)_2]$ X contains low-spin iron(II) and high-spin iron(III) in octahedral environments. In this case the  $t_{20}(Fe(II)) \rightarrow$ t<sub>20</sub>(Fe(III)) transition is observed at 1680 nm. The band is very intense ( $\epsilon \sim 8000$  in colloidal suspension). The linear cyanide bridge Fe(II)-C=N-Fe(III) provides an effective pathway (via  $\pi$ orbitals) for electron (t<sub>2g</sub>) delocalisation. <sup>36</sup> Further each iron(II) electron can jump to any one of the six adjacent iron(III) sites.

In  $[Fe(Fe(aao)_3)_2]X$ , we have not been able to locate any distinctive intervalence band. The delocalisation of the  $t_{2g}$  electrons via the N-O bridge in the proposed stereochemistry (Fig. V.7) will be much less than that through CN bridge in

Prussian blue. Then there is a very strong  $iron(II) \rightarrow ligand$  transition centred at  $\sim 600$  nm. The intensity of this band is quite large even at 700 nm ( $\epsilon \sim 11,000$ ) and beyond (Fig. V.8). These factors may be responsible for the failure to observe the intervalence band.

#### g. Some Related Species

Preliminary results on two systems will be briefly stated here, since these have some bearings on the structural problem at hand.

Attempted synthesis of the bromide analogue of  $[\text{Fe(Fe(aao)}_3)_2].\text{FeCl}_4$  (by replacing  $\text{FeBr}_3$  for  $\text{FeCl}_3$  in the synthetic method) led to a product which had all the properties expected of  $[\text{Fe(Fe(aao)}_3)_2]\text{Br}.$  In the region 500-300 cm<sup>-1</sup> it shows only the Fe-O stretch ( $^{\circ}420$  cm<sup>-1</sup>).

NaFe(aao)<sub>3</sub>.H<sub>2</sub>O reacts with Ni(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O in ethanol to give a non-electrolytic product which can be formulated as Ni[Fe(aao)<sub>3</sub>]<sub>2</sub>. Apart from showing the intense Fe(aao)<sub>3</sub> bands ( $\sim$  600 nm; 440 nm) it exhibits a weak broad band at  $\sim$ 1390 nm which may be due to the presence of nickel in a very weak octahedral ligand field ( $v_1$  transition). Our speculation is that its structure is similar to that of [Fe(Fe(aao)<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (Fe<sup>3+</sup> replaced by Ni<sup>2+</sup>).

#### E. EPR Spectra

The room temperature powder epr spectra of two  $[\text{Fe}(\text{Fe}(\text{aao})_3)_2].\text{ClO}_4$  complexes are displayed in Fig. V.9. The most characteristic feature is an absorption with an apparent g value  $(g^i)$  of  $\sim 4.3$ . This strongly suggests a rhombic geometry for the  $\text{FeO}_6$  coordination sphere. The system  $[\text{Fe}(\text{Fe}(\text{aao})_3)_2]$ Br behaves similarly (Fig. V.10).

The polycrystalline epr spectra of rhombically distorted octahedral high-spin  ${\rm Fe}^{3^+}({\rm d}^5)$  have been the subject of many investigations. The  ${\rm S}=\frac{5}{2}$  state splits into three Krammer doublets  $({\rm S}_{\rm Z}=\pm\frac{1}{2}$ ,  $\pm\frac{3}{2}$ ,  $\pm\frac{5}{2}$ ). The eigen functions are actually a mixture of the three doublets, the extent of mixing depends on the parameter  $\lambda$ = E/D. The spin Hamiltonian usually used to fit the spectra is

$$\mathcal{H}_{s} = g \beta H \cdot \bar{s} + D \left[ s_{z}^{2} - \frac{1}{3} s(s+1) \right] + E(s_{x}^{2} - s_{y}^{2})$$
 (9)

The parameter  $\lambda$  is a measure of the rhombic character of the crystalline environment. The maximum possible (i.e., perfect) rhombic symmetry in the crystalline field occurs as  $\lambda = \frac{1}{3}$  ( $\lambda = 0$  or 1 corresponds to perfect axial symmetry). For the  $S = \frac{5}{2}$  system six energy levels are present in a magnetic field (levels 1, 2, 3, 4, 5, 6 in order of increasing energy). A sizable number of transitions are thus possible and are often observed spread over a wide range of field (typically 600-8000 G in the X-band).

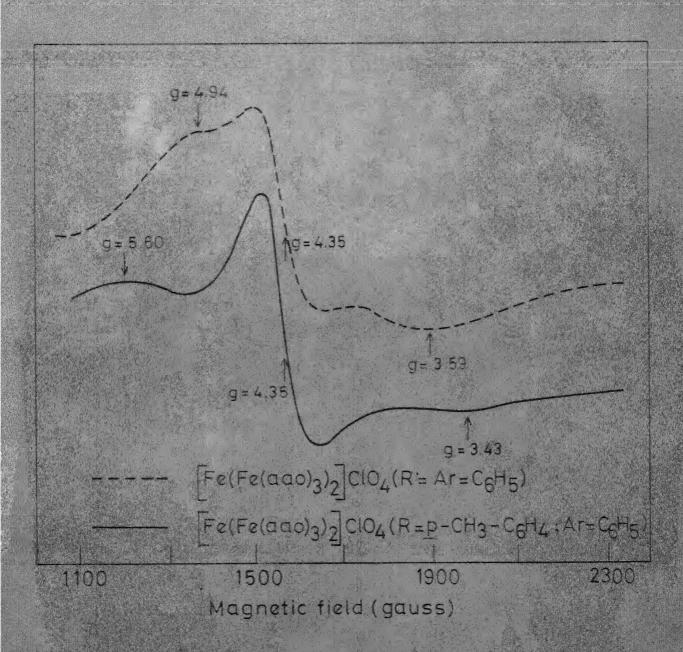


FIG. V. 9 POWDER ELECTRON SPIN RESONANCE SPECTRA

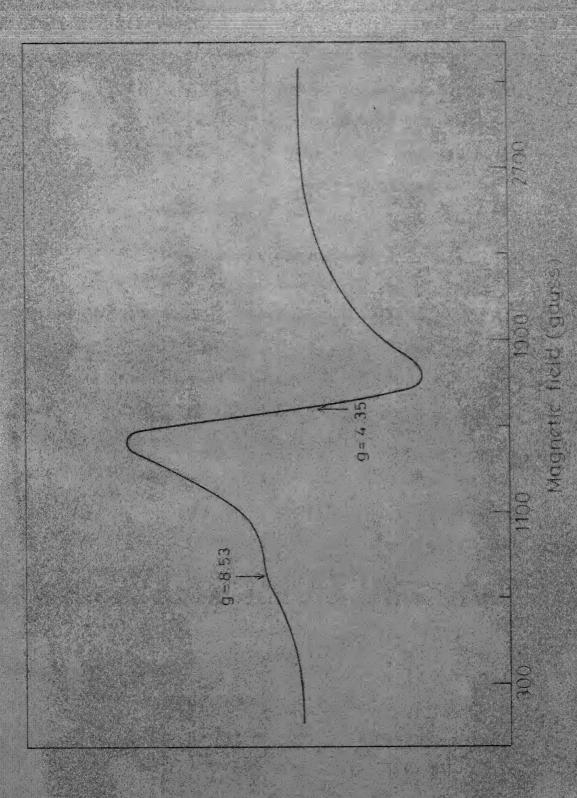


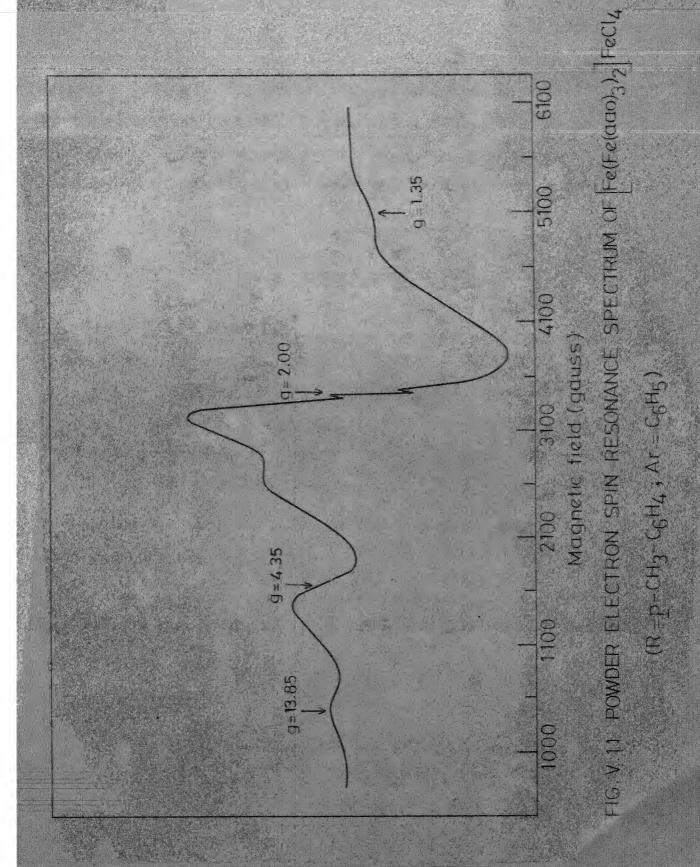
FIG. V 10. POWDER ELECTRON SPIN THE SCHLAMET SET OTHUM OF HEIFEGOODY DE (R=At=Cg15)

However, the most intense and therefore the most characteristic of all is a transition (level  $3 \rightarrow 4$ ) with  $g' \sim 4.3$ . This absorption is isotropic at  $\lambda = \frac{1}{3}$ . Deviation of  $\lambda$  from  $\frac{1}{3}$  brings in anisotropy which is reflected in the experimental spectrum as a broadening or splitting  $^{38,39,42}$  of the  $g' \sim 4.3$  transition. The  $g' \sim 4.3$  absorption has been used as a signature of perfect or nearly perfect rhombic symmetry in pseudooctahedral Fe<sup>3+</sup> species.

Our comment that the epr spectrum of  $[Fe(Fe(aao)_3)_2]x$ ,  $(x=ClO_4, Br)$  suggests a rhombic geometry for the  $FeO_6$  coordination sphere has to be viewed in the light of above discussion. The observed spectra are comparable to those of other rhombic  $FeO_6$  systems such as sideramines  $^{4O}$  and Ferrichrome-A (ref. 39). The  $[Fe(Fe(aao)_3)_2]$ .  $FeCl_4$  again shows an absorption at  $g' \sim 4.3$  (Fig. V.11). This absorption is partially superposed on a more intense isotropic absorption at  $g \sim 2$  transition characteristic of tetrahedral  $FeCl_4$ . The epr spectrum (Fig. V.11) provides an additional evidence for the suggested formulation  $[Fe(Fe(aao)_3)_2]$ .  $FeCl_4$ . A more detailed analysis of the epr spectra of all  $[Fe(Fe(aao)_3)_2]x$  systems is in progress.

#### F. Conclusion

It is demonstrated that the Haao ligand can strongly bind iron(II) via azoimine chelation. The resulting  $Fe(aao)_3$  species appears to have a <u>cis</u> stereochemistry. The  $Fe(aao)_3$  unit acts as a versatile donor by virtue of the oximato oxygen atoms. It



binds H, Na, Ni<sup>2+</sup> and Fe<sup>3+</sup> (and a variety of other cations not discussed in this thesis). Mössbauer studies of the various systems would be quite interesting and would throw further light on the structural problem. Due to lack of facilities we have not been able to undertake such studies so far. We now plan these studies in collaboration with some laboratories elsewhere.

### V.3 EXPERIMENTAL SECTION

### A. Preparation of Compounds

#### a. Chemicals

Acetaldehyde was prepared by decomposing paraldehyde with a few drops of  ${\rm H_2SO_4}$  (concentrated) and carefully distilling it. Commercial <u>n</u>-butraldehyde, benzaldehyde, and <u>p</u>-tolualdehyde were used as such or after distillation.

 $\underline{n}$ -Butylnitrite was prepared by reacting  $\underline{n}$ -butylalcohol with nitrous acid.

Commercial anhydrous iron(III) chloride was used in the reactions. Iron(II) perchlorate was prepared from iron powder and perchloric acid.

#### b. Ligands

Arylazooximes were prepared by the nitrosation of aldehydearylhydrazone using butyl nitrite. The details are as follows:

### i. Preparation of Aldehydephenylhydrazones

Phenylhydrazones of benzaldehyde and p-tolualdehyde were prepared by shaking aldehyde with phenylhydrazine (in 1:1 molar ratio) in acetic acid(20%). Pale yellow solid-formed was collected by filtration, washed with very dilute acetic acid, water-ethanol mixture and dried at  $60^{\circ}\text{C}$ ).

Acetaldehydephenylhydrazone was prepared according to the procedure of Bamberger<sup>1</sup> with a little modification. The reaction was carried out at 0°C rather than at 10°C. In this way shining white crystals of hydrazone resulted with greater ease.

<u>n</u>-Butraldehydephenylhydrazone was prepared as follows:

0.2 mol of <u>n</u>-butraldehyde was cooled to subzero temperature in a freezing mixture. 0.2 mol of phenylhydrazine was added dropwise with continuous stirring and keeping the reaction mixture always below 0°C during the addition. The mixture was allowed to stand for another 15 min. 10 g of anhydrous sodium sulphate was then added. An orange oil separated which was collected and used as such.

### ii. Arylazooximes from Aldehydephenylhydrazones

Arylazooximes with R= alkyl were prepared as follows: 0.03 mol of phenylhydrazone was dissolved in 30 ml ether. 0.2 mol of <u>n</u>-butylnitrite was added to the above solution which was then kept at room temperature. The reaction mixture which had turned dark reddish brown was extracted with 3x35 ml of 0.5 N aqueous sodium hydroxide. The aqueous extract was cooled to  $0^{\circ}$ C and was then neutralised by dropwise addition of cold  $1\,\mathrm{N}\,\mathrm{H}_2\mathrm{SO}_4$ . During this process colour of the solution became progressively lighter and towards the end arylazooxime separated out as an orange crystalline solid. The orange solid was filtered, dried and the recrystallised from hexane. Yield was 25%.

Arylazooximes with R= aryl were synthesised as described below: 0.1 mol of phenylhydrazone was dissolved in 150 ml of methanol (AnalaR grade). 0.2 mol of n-butylnitrite was added to it followed by 0.15 mol of potassium tertiary butoxide (or 0.2 mol of sodium methoxide). Immediately a red colouration developed. This mixture was heated to reflux for 1/2 hr and then cooled to room temperature and filtered. To the filtrate was added 0.15 mol of NaOH in 300 ml water. The mixture was kept for 4 hr in refrigerator and then extracted with ether. The aqueous layer was cooled to 0°C and neutralised with cold 1 N H<sub>2</sub>SO<sub>4</sub>. The yellow crystalline solid formed was filtered, dried and recrystallised from hexane-dichloromethane mixture. Yield was 40%.

### c. Preparation of $[Fe(Fe(aao)_3)_2]FeCl_4$

Haao (0.015 mol) was dissolved in 30 ml ethanol (95%) and to it was added an ethanolic solution of anhydrous iron(III) chloride (0.01 mol in 20 ml). Immediately the colour darkened. The mixture was heated to boil. A crystalline solid started separating. The mixture was then cooled and filtered. The black

crystalline solid was washed thoroughly with benzene and then recrystallised from chloroform-ethanol mixture. The yield was 40%. However, we could not isolate a similar product when Haao with  $R=CH_2$  was used.

### d. Conversion of [Fe(Fe(aao) $_3$ ) $_2$ ]FeCl $_4$ to NaFe(aao) $_3$ .H $_2$ O

[Fe(Fe(aao)<sub>3</sub>)<sub>2</sub>]FeCl<sub>4</sub> (0.01 mol) was dissolved in 100 ml acetone and to it an aqueous solution of sodium hydroxide (0.03 mol in 15 ml water) was added dropwise. The mixture was warmed and stirred for 10-15 min. The mixture turned green and a brown precipitate of ferric hydroxide also deposited. The green solution was filtered, and the filtrate was concentrated. Shining green needle like crystals separated. These were collected by filtration and were recrystallised from acetone mixed with a very dilute aqueous sodium hydroxide.

### e. Regeneration of [Fe(Fe(aao)3)2]FeCl4 from NaFe(aao)3.H2O

NaFe(aao) $_3.H_2$ O(0.002 mol) was dissolved in 25 ml ethanol (95%) and to it was added an ethanolic solution of anhydrous iron(III) chloride (0.002 mol in 5 ml). The colour immediately turned greenish black. A black crystalline solid separated. This was found to be identical to  $[Fe(Fe(aao)_3)_2]FeCl_4$ .

### f. Preparation of HFe(aao)3 from NaFe(aao)3.H20

 $NaFe(aao)_3.H_2O$  (0.002 mol) was dissolved in 50 ml aqueous ethanol (50%). To this 0.0025 mol of HCl in 10 ml water was

added dropwise with stirring. Black precipitate of HFe(aao)<sub>3</sub> resulted. This was collected by filtration, washed several times with water and was then dried.

# g. Conversion of HFe(aao)3 to NaFe(aao)3.H2O

 $\mathrm{HFe(aao)}_3$  (0.002 mol) was dissolved in 15-20 ml acetone and an aqueous solution of sodium hydroxide (0.003 mol in 5 ml water) was added dropwise. The mixture turned green in colour. Gradual evaporation of acetone yielded shining green crystals of NaFe(aao) $_3.\mathrm{H}_2\mathrm{O}$ .

### h. Conversion of HFe(aao) $_3$ to [Fe(Fe(aao) $_3$ ) $_2$ ]FeCl $_4$

HFe(aao) $_3$  (0.002 mol) was taken in 50 ml ethanol and to it was added an ethanolic solution of anhydrous iron(III) chloride (0.002 mol, 5 ml). The mixture was heated to boil for 15 min. Shining black crystals of [Fe(Fe(aao) $_3$ ) $_2$ ]FeCl $_4$  were obtained.

### i. Preparation of NaFe(aao)<sub>3</sub>. $H_2$ O for R = $CH_3$

Phenylazoacetaldoxime (0.03 mol) was dissolved in 50 ml ethanol (95%). An ethanolic solution of iron(III) chloride (0.02 mol) (or freshly prepared iron(III) acetate) was added to it. The reaction mixture was heated to boil. The black colour of the mixture deepened and a gummy mass separated. This was suspended in 40 ml of ethanol and treated with 0.03 mol of aqueous sodium hydroxide. An immediate green solution was obtained. The mixture

was warmed a little and filtered. The green solution was evaporated to dryness and was recrystallised from acetone-hexane or chloroform-hexane mixture. Shining green crystals were obtained in 50% yield.

## j. Preparation of $[Fe(Fe(aao)_3)_2]Clo_4$

Haao (0.03 mol) was dissolved in 30 ml ethanol and to it was added an ethanolic solution iron(II) perchlorate (0.015 mol in 30 ml). Immediately the colour darkened. The mixture was heated to boil. A black crystalline solid settled on cooling. This was washed with benzene and then recrystallised from chloroform-ethanol mixtures. The yield was 40%.

# k. Conversion of $[Fe(Fe(aao)_3)_2]Clo_4$ to NaFe(aao)\_3.H2O

[Fe(Fe(aao)<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> (0.01 mol) was dissolved in 100 ml acetone and to it an aqueous solution of sodium hydroxide 0.03 mol in 15 ml water) was added dropwise. The mixture was warmed and stirred for 10-15 min. The mixture turned green and a brown precipitate of ferric hydroxide also deposited. The green solution was filtered and acetone was evaporated gradually. Shining green crystals of NaFe(aao)<sub>3</sub>.H<sub>2</sub>O were obtained.

# 1. Regeneration of [Fe(Fe(aao)<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> from NaFe(aao)<sub>3</sub>.H<sub>2</sub>O

NaFe(aao)<sub>3</sub>.H<sub>2</sub>O (0.002 mol) was dissolved in 25 ml ethanol and to it was added an ethanolic solution of iron(III) perchlorate (0.001 mol in 5 ml). The colour immediately turned greenish

black. The mixture was heated to boil for 10 min. Black crystals of  $[Fe(Fe(aao)_3)_2]Clo_4$  resulted.

### B. Characterization of Complexes

This was done by C, H, N micro analyses and by metal analyses. Characterization data for all compounds are collected in Table V.12. Total iron was estimated gravimetrically as described in Chapter IV.

# a. Amount of iron rejected from $[Fe(Fe(aao)_3)_2]FeCl_4$ and $[Fe(Fe(aao)_3)_2]Clo_4$ on addition of sodium hydroxide

NaOH was dissolved in 2 ml water and was added dropwise to the above solution. The mixture was stirred magnetically for 15 min and was then filtered through a sintered crucible. Four to five drops of sodium hydroxide solution was added to the filtrate and the mixture was filtered again to ensure the complete removal of ferric hydroxide rejected in the reaction. The ferric hydroxide was transfered to a beaker and was dissolved in 1 N HCl. 1.5 g of ammonium acetate in 70 ml water was added, followed by oxine reagent (2% in 1 N acetic acid) from a burette with constant stirring until a slight excess was present. About 6-7 ml was required. The dark precipitate thus obtained was digested on water-bath for 1 hr. It was filtered through a preweighed sintered crucible and washed successively with 1% acetic acid and water. It was dried

TABLE V.12

CHARACTERIZATION DATAB

-	The second secon								
Com	Compound	Calcd	%C Found	Calcd F	H Found	Calcd	%N Found	Calcd	%Fe Found
	NaFe(aao) <sub>3</sub> ·H <sub>2</sub> o <sup>b</sup>		Andrew dat turnstallent krafter grant gestellt der	reminents of exceptions of the contract of the	desirent between the control of the	and the same of th	akin memanan pada inga kanganan pada pada pada pada pada pada pada	Pijderandi Benjaranjerana razanska	
1	1) $R = CH_3$	49,40	50.18	4.46	5.10	21.61	21.70	9.57	8.72
2)	2) $R = D^{-}C_3H_7$	53,97	53,21	5.69	5.52	18.89	19,03	8,39	7.92
3)	3) $R = C_6 H_5$	98.09	60.30	4.15	4.20	16.38	16.70	7,28	7.20
4)	4) $R = \underline{p} - CH_3 - C_6 H_4$	62.17	61.78	4.69	4.60	15.54	15,50	6.91	6.19
	HFe(aao) <sub>3</sub>								
5)	5) $R = n - C_3 H_7$	57.50	57.42	5.68	5,80	20.09	19.80	ı	1
(9	$6) R = C_6 H_5$	64.21	63.78	4.21	4.32	17.29	16.91	ì	i
1)	7) $R = P - CH_3 - C_6 H_4$	65.37	64.69	4.80	5.09	16.34	15,91	7,35	6.82
	[Fe(Fe(aao) <sub>3</sub> ) <sub>2</sub> ] <sup>F</sup>	2]Fec14							
8		47,80	47.53	4,78	4,85	16.73	16,90	14,80	14,49
6	9) R=C <sub>6</sub> H <sub>5</sub>	54.73	54.46	3,51	3.71	14.73	14,55	13,01	13,05
10)	10) $R = p - CH_3 - C_6 H_5$	56,18	57.04	4.01	4.36	14,04	13.79	12.46	12.56
								S	contd.

TABLE V.12 (CONTD.)

	%	%C	H %	田	N %	Z	% Fe	ът О
Compound	Calcd	Calcd Found	Calcd	Calcd Found	Calcd	Calcd Found	Calcd	Calcd Found
	infigural terrai förgrafiganspialspal de de de afgelikt symfat fälle afgelikt.				Andrea Communication of the Co			
[Fe(Fe(aao)3)	2]Clo4							
man and the second property of the second pro								
11) $R = C_6 H_5$	58.09	58.09 57.91	3.75	3,75 3,85	15.64	15.64 15.44	10.53 10.59	10.59

a. In all the compounds  $Ar=C_6H_5$ 

b. Percentage sodium in compounds (2) and (3), Calcd: 3.54 & 2.99; Found: 3.71 & 2.81 respectively. c. Percentage chloride in compounds (9) and (10), Calcd: 8.34 & 7.93; Found: 8.12 & 7.59 respectively. at  $125-135^{\circ}$ C to constant weight and weighed as Fe(C<sub>6</sub>H<sub>6</sub>OH)<sub>3</sub>.

### $[Fe(Fe(aao)_3)_2]FeCl_4$

Percentage of total iron present = 13.05%

Weight of the compound taken for the iron rejection expe-

riment

Weight of the iron oxinate = 0.06172 g

= 0.10702 g

Percentage of iron rejected = 6.69%

Total iron in the complex =  $\frac{13.05}{6.59} = 1.98$ 

### $[Fe(Fe(aao)_3)_2]Clo_4$

Percentage of total iron present = 10.53%

Weight of the compound taken for the iron rejection expe-

for the iron rejection experiment

riment = 0.17265 g

Weight of the iron oxinate = 0.05280 g

Percentage of iron rejected = 3.49%

Total iron in the complex =  $\frac{10.53}{3.49} = 3.01$ 

### b. Estimation of Sodium 46

100 mg of NaFe(aao)<sub>3</sub>.H<sub>2</sub>O was dissolved in 40 ml distilled water. 1N HCl was added till the green colour completely disappeared (the solid is HFe(aao)<sub>3</sub>; Na remains in solution). The colourless solution was filtered and the residue was washed with water. The filtrate and the washings were collected in a Chinadish and 8 ml of zincuranylacetate reagent was added. The

mixture was stirred magnetically for 1 hr and was then allowed to stand for 2 hr. An yellow crystalline precipitate thus obtained was filtered through a preweighed sintered crucible. The precipitate and the inside of crucible were washed thoroughly with washing solution and then once with ether. Air was drawn through the crucible to remove ether. The crucible was wipep with moist cloth and placed in the desiccator for 1 hr and weighed, as  $NaZn(UO_2)_3(C_2H_3O_2)_9.6H_2O$ . The weight was corrected as indicated by a blank determination carried through all steps of the above method.

Preparation of the reagent: 2 g of UO<sub>2</sub>(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>.2H<sub>2</sub>O and 5.56 g of zinc acetate was dissolved in O.55 ml glacial acetic acid and 18 ml water. The solution was warmed until no further dissolution occurred, and was then cooled. A small precipitate of sodium salt precipitated out (impurity). The solution was allowed to stand for 24 hr and then filtered. Precaution was taken that the reagent was used at approximately the temperature prevailing at the time it was filtered.

Preparation of washing solution: Washing solution was prepared by adding 1 ml of acetic acid (30%) to 100 ml of ethanol (95%), shaking with a moderate excess of the triple salt,  $NaZn(UO_2)_3$ -  $(C_2H_3O_2)_9.6H_2O$  at room temperature and filtering.

### $NaFe(aao)_3.H_2O(R=Ar=C_6H_5)$

Weight of the compound taken for sodium analysis

= 0.11245 g

Weight of  $NaZn(UO_2)_3(C_2H_3O_2)_9$ .

= 0.21148 g

Percentage of sodium 2.81%

Calculated percentage of

2.99% sodium

#### c. Chloride Estimation

80 mg of [Fe(Fe(aao)<sub>2</sub>)<sub>2</sub>]FeCl<sub>4</sub> was taken in a nickel cruci-2 g of powdered potassium hydroxide and 1 g of potassium nitrate were added. The mixture was warmed slowly till it formed a melt. The melt was heated rigorously for another 20 minutes. The fused mass was extracted with water and filtered through a sintered funnel. The sintered funnel was washed with water several times. The filtrate and washings were collected together and acidified with dilute nitric acid. A solution of 0.1 N AgNO3 was then added dropwise till the precipitation was complete. The precipitate of AgCl was filtered through a preweighed sintered crucible and was washed 3-4 times with very dilute nitric acid and dried in hot air oven at 110°C.

#### C. Solvents

Details are given in Chapter II.

#### D. Physical Measurements

### a. Electrical Conductance Measurements

Details are given in Chapter II.

### b. Infrared Spectra

Details are given in Chapter II.

For the region 500-300  ${\rm cm}^{-1}$  spectra were recorded in nujol mull using polyethylene windows.

### c. Electronic Spectra

Details are given in Chapter II.

### d. Bulk Susceptibility Measurements

Details are given in Chapter II.

#### e. Electron Spin Resonance Spectra

Details are given in Chapter II.

### f. Proton Magnetic Resonance Spectra

Pmr spectra were recorded at 100 MHz using a Varian HR-100 Spectrometer. Frequencies were measured by the usual side band technique. CDCl<sub>3</sub> was used as solvent and tetramethylsilane was used as an internal standard. Area measurements, where necessary were achieved Planimetrically.

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### SUMMARY

The chemistry described in this thesis can be broadly divided under two categories (i) mixed-ligand type and (ii) mixed-metal type. The materials presented in Chapters I-IV belong to the category (i), while those in Chapter V fall under category (ii).

I

A monomeric complex of formula M(Lb)(Lt) (where Lb and Lt are potentially bidentate and tridentate ligands) in which all potentially coordinating atoms are bonded to metal will be pentacoordinated. In recent times this strategy has been used in our laboratory and elsewhere to design interesting systems. Not infrequently the M(Lb)(Lt) system dimerises yielding pseudo-octahedral coordination. In other instances, adduct formation with donors bring about the same coordination geometry. In several cases the equilibrium between hexacoordinated and pentacoordinated geometry has been identified in solution. This area is reviewed in Chapter I.

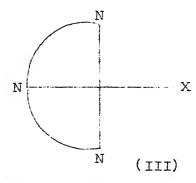
A new structural situation is described in Chapter II in which the ligand systems involved are pyrrole-2-aldehyde (Hpyr) and its Schiff base with  ${\rm H_2N-(CH_2)}_{\rm n}{\rm -NR_2}$  (n = 2 or 3). The conjugate base of these species are shown in I and II. I will abbreviated as pyr, while the abbreviation for II will be pyrenNR<sub>2</sub>

$$(I) \qquad \qquad N \qquad \qquad N$$

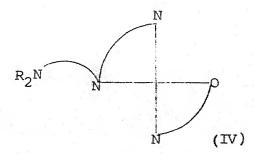
(when n = 2) and  $pyrtnNR_2$  (when n = 3). The following systems have been obtained in the present work:  $M(pyrenNR_2)Br$ ,  $M(pyrtnNR_2)Br$ ,  $M(pyr)(pyrenNR_2)$ ,  $Cu(pyr)(pyrtnNR_2)$  (M = Cu or Ni).

M(pyrenNR<sub>2</sub>)Br and M(pyrtnNR<sub>2</sub>)Br: The nickel(II) system is diamagnetic while the copper(II) complexes have normal magnetic moment of ~1.8 BM. This and spectral results suggest the structure III. The most important point to note here is that both the ligand systems pyrenNR<sub>2</sub> and pyrtnNR<sub>2</sub> act in the tridentate fashion. The electrical conductivity data suggest that the compounds undergo partial dissociation in solution, probably due to reactions of the type

$$M(pyrenNR_2)Br + \underline{n}-CH_3NO_2 \rightleftharpoons M(pyrenNR_2)(CH_3NO_2)_n^+ + Br^-$$
 (1)



M(pyr)(pyrenNR<sub>2</sub>): The infrared spectrum of Cu(pyr)<sub>2</sub> shows the C=O stretch at 1650 cm<sup>-1</sup>, while Cu(pyrenNR<sub>2</sub>)Br system described earlier, has the C=N stretch at ~ 1600 cm<sup>-1</sup>. As expected the M(pyr)(pyrenNR<sub>2</sub>) systems show both C=O and C=N stretches. Cu(pyr)-(pyrenNEt<sub>2</sub>) was found to be monomolecular in freezing benzene. The mixed complexes could be either pentacoordinated belonging to the class M(Lb)(Lt) with all potential donor sites bound to the metal or tetracoordinated and planar with bidentate pyrenNR<sub>2</sub> as in IV (NR<sub>2</sub> group is not coordinated to the metal). These complexes have normal magnetic moments. Ligand field spectra and ir data indicate that this system is actually tetracoordinated.

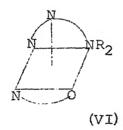


More definitive evidence in favour of structure IV is obtained from studies of mixed crystal of Cu(pyr)(pyrenNMe<sub>2</sub>) and Ni(pyr)(pyrenNMe<sub>2</sub>). The most important observation is that the

mixed crystals are isomorphous with pure Cu(pyr)(pyrenNMe2), as determined from X-ray powder patterns and d-spacings. Since Ni(II) is diamagnetic and planar (IV) in the mixed crystal, it follows that the copper(II) species has also the geometry (IV) in the mixed crystal. Because of isomorphism, this is also true for the pure copper(II) complex. Thus Cu(pyr)(pyrenNMe2) has the planar environment IV. Very dilute solution of Cu(pyr)(pyrenNMe2) in Ni(pyr)(pyrenNMe<sub>2</sub>) shows an axial epr spectrum with  $g_{11} = 2.199$ ;  $g_{\parallel} = 2.045$  and  $A_{\parallel} = 187.0$  gauss;  $A_{\perp} = 6.0$  gauss. Earlier we have categorised the various ways (dimerisation, adduct formation) by which pentacoordination may be hindered in a M(Lb)(Lt) system. The pyrrole-2-aldimine species described above, provide example of a new situation where the potentially tridentate unit, actually acts only as bidentate ligand. We strongly suspect that the phenomenon is of steric origin. The ligand pyren $NR_2$  in its tridentate mode will be able to span only in the meridional fashion due to the short length of the -(CH2)2- chain. Models show that this brings the bidentate pyr moiety unfavourably close to the methyl groups of NMe, in pyrenNMe, in the hypothetical square pyramidal structure V. This steric hindrance leads to

the delinking of NMe, from the metal atom.

 ${\rm Cu(pyr)\,(pyrtrNR_2)}:$  If the above thesis regarding the steric effect in M(pyr)(pyrenNR\_2) is correct, the complexes Cu(pyr)-(pyrtnNR\_2) with a more flexible -(CH\_2)\_3- chain may be pentacoordinated. In this potentially tridentate ligand can span facially. Models show that the configuration VI, is free from steric strain. With these ideas in mind the Cu(pyr)(pyrtnNR\_2)



complexes were synthesised. They are monomolecular and have normal magnetic moments and ir spectra. Their d-d electronic spectra strongly suggest pentacoordinate geometry.

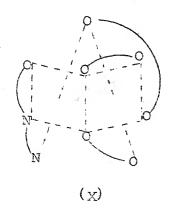
#### III

In our search for the pentacoordinated species of the type  $\operatorname{Ni(Lb)}(\operatorname{Lt})$ , the reaction of bis(acetylacetonato)nickel(II),  $\operatorname{Ni_3(ac)_6}$ , with  $\operatorname{HsalenNR_2}$  was investigated earlier (ac and  $\operatorname{salenNR_2}$  are respectively the conjugate bases of acetylacetone (VII) and the Schiff base (VIII) of salicylaldehyde and  $\operatorname{H_2N-(CH_2)_2-NR_2}$ ). Square pyramidal species of the type  $\operatorname{Ni(ac)-(salenNR_2)}$  were obtained. Having observed the dramatic stereochemical consequence of the  $\operatorname{-(CH_2)_n-chain length}$  in pyrrole-2-

aldimine complexes, we undertook the investigation of the effect of this chain length on the composition and stereochemistry of some nickel(II) species. The systems, obtained by reacting  $\text{Ni}_3(\text{ac})_6$  with  $\text{HsaltnNR}_2$  (IX) are reported in Chapter III. These

$$\sim$$
 OH  $\sim$  NR<sub>2</sub>  $\sim$  (IX)

systems are of the type  $\mathrm{Ni}_2(\mathrm{ac})_3(\mathrm{saltnNR}_2)$ . From magnetic susceptibility, ir and electronic spectral data it is concluded that each nickel(II) is in a pseudooctahedral environment. On the basis of model building it is proposed that  $\mathrm{Ni}_2(\mathrm{ac})_3(\mathrm{saltnNR}_2)$  has the structure  $\mathrm{X}$  in which ac occupies bridging positions. It is known that the dinuclear fragment  $\mathrm{Ni}_2(\mathrm{ac})_4$  is coordinatively unsaturated and yields adducts such as  $\mathrm{Ni}_2(\mathrm{ac})_4(\mathrm{pyridine})$  in which nickel(II) is octahedral. One may then expect that species of the type  $\mathrm{Ni}_2(\mathrm{ac})_3(\mathrm{tridentate})$  with octahedral nickel(II) should exist. The  $\mathrm{Ni}_2(\mathrm{ac})_3(\mathrm{saltnNR}_2)$  system provides an example. We have

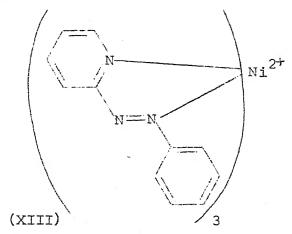


noted earlier that the reaction of  $\mathrm{Ni_3(ac)_6}$  with  $\mathrm{salenNR_2}$  yields mononuclear pentacoordinate  $\mathrm{Ni(ac)(salenNR_2)}$ . No evidence for dinuclear species has been obtained with this ligand. The difference in the behaviour of  $\mathrm{salenNR_2}$  and  $\mathrm{saltnNR_2}$  can be rationalised on the basis of structure X. In this structure  $\mathrm{saltnNR_2}$  occupies three facial positions of an octahedron. The flexible  $-(\mathrm{CH_2})_3$ — chain makes this possible. On the other hand  $\mathrm{salenNR_2}$  can only span in meridional positions due to relative shortness of the  $-(\mathrm{CH_2})_2$ — chain. It cannot span facially.

IV

In Chapters IV and V the ligand systems used contain an azo group or more appropriately azoimine group XI. The results

obtained with 2-phenylazopyridine (pap) XII, form the subject matter of Chapter IV. The tris complexes  $\mathrm{Ni(pap)}_3(\mathrm{Clo}_4)_2$  and  $\mathrm{Fe(pap)}_3\mathrm{I}_2$  (these are not mixed-ligand complexes) behave as 1:2 electrolyte in solution. They contain the complex cation  $\mathrm{M(pap)}_3^{2^+}$ .  $\mathrm{Ni(pap)}_3^{2^+}$  is fully paramagnetic and on the basis of electronic spectra has the octahedral structure XIII, with  $\mathrm{NiN}_6$ 



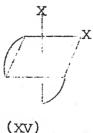
coordination sphere. Fe(pap) $_3^{2^+}$  is low-spin and is believed to have a similar structure. It shows an intense band in the visible region ( $\sim 590$  nm) which is assigned to the charge transfer transition  $t_{2g}^{-\to}\pi^*$  (azoimine). The isoelectronic relationship between azoimine and diimine XIV, fragments are noted in this

-N=C-C=N-

(XIV)

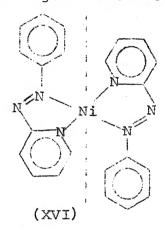
context. The  $t_{2g} \rightarrow \pi^*$  state also makes some contribution to the ground level also as is evident from ir data. The N=N stretch is considerably lowered in Fe(pap) $_3^{2^+}$  in comparison to those in the free ligand and the nickel(II) complex.

Nickel(II) forms mixed complexes of the type Ni(pap) $_{2}^{X}$ ,  $\text{O.5CH}_2\text{Cl}_2$  (X = Cl, Br). These are fully paramagnetic in solid state and are only very slightly dissociated in solution. There is evidence that in systems of the type Ni(Lb)2X2 (where Lb is a bidentate ligand), the cis configuration is preferred over the trans configuration, when X is widely separated from Lb in the spectrochemical series. In going from NiN, to trans -NiN,X, the octahedral  $\nu_1$  band shows an observable splitting due to decrease in symmetry from  $\mathbf{O_h}$  to  $\mathbf{D_{4h}}$ . The  $\underline{\mathbf{cis}}\mathbf{-NiN_4}\mathbf{X_2}$  sphere has a lower symmetry ( $C_{2v}$ ) than  $\underline{\text{trans}}\text{-NiN}_4X_2$  but the magnitude of orbital splitting is expected to be less. In practice such splitting is often not observed. The complexes of 2-phenylazopyridine under discussion shows an unsplit  $v_1$  band at 1090 nm. This taken in conjunction with other evidences has led us to propose the structure XV for Ni(pap) 2X2,0.5CH2Cl2 species. The dichloromethane of crystallisation is strongly held in the



lattice and is not removed even at low pressure (5 mm) and elevated temperature (80°C). Quite a few transition metal complexes which contain dichloromethane of crystallisation are known. We wish to stress that the present compounds can also be prepared as amorphous powders without the dichloromethane of crystallisation.

On the other hand well formed crystals which are easy to purify are obtained when dichloromethane is present. The solid state infrared spectra of  $\mathrm{Ni}(\mathrm{pap})_2\mathrm{Br}_2$  and  $\mathrm{Ni}(\mathrm{pap})_2\mathrm{Br}_2$ ,  $0.5\mathrm{CH}_2\mathrm{Cl}_2$  were found to be essentially superimposable except that the latter compound shows bands characteristic of dichloromethane also. The dichloromethane of crystallisation does not appear to affect the ligand disposition in any major way. Now we turn to  $\mathrm{Ni}(\mathrm{pap})_2\mathrm{I}_2$  which is diamagnetic and shows no ligand field bands below 700 nm. In this complex the  $\mathrm{Ni}(\mathrm{pap})_2$  sphere is grossly planar presumably with a trans (steric overcrowding of phenyl groups in cis geometry) disposition of ligand molecules XVI. The iodide ions



remain partially bound (weak axial coordination) in solution, since the observed electrical conductivity is much lower than that expected for a 1:2 electrolyte. In view of the proposed difference in stereochemistry of Ni(pap)<sub>2</sub> fragment in the chloro (or bromo) and iodo complexes, it may be significant that the -N=N- stretch in former (no centre of symmetry) is more intense than that of the latter (centre of symmetry).

In the last chapter (Chapter V) mixed-metal complexes of the type XVII, (where M and M' could be two different metal ions or it could be the same metal ion in two different oxidation states) derived from arylazooximes (Haao) XVIII, are described. This class of

$$C = N$$
 $O = M$ 
 $R = C (=NOH) - N = NAr$ 
 $(XVII)$ 
 $(XVIII)$ 

ligand has a strong affinity for iron(II). The low-spin ( $t_{2g}^6$ ) anionic tris chelate Fe(aao) $_3$  contains five membered chelate rings (ir data), XIX and is green in colour due to the presence

of a strong  $t_{2g} \to \pi^*$  (azoimine) charge-transfer transition at  $\sim 600$  nm. This ion can be isolated in the form of a sodium salt  $\text{NaFe(aao)}_3.\text{H}_2\text{O}$  in which  $\text{Fe(aao)}_3$  has (pmr data) <u>cis</u> geometry XX.

The sodium ion is believed to be bound to water molecule and to oximato oxygen atoms as slown schematically in structure XXI.

NaFe(aao)<sub>3</sub>.H<sub>2</sub>O is poorly conducting in nitromethane solution.

It is soluble in a variety of organic solvents including benzene.

On reaction with acid it produces HFe(aao) $_3$  in which the proton is believed to be chelated (intermolecularly or intramolecularly) to Fe(aao) $_3^-$  via the oxime oxygen atoms.

Our researches in iron complexes of arylazooximes originated from the attempted reaction of Haao with anhydrous  ${\rm FeCl}_3$  in ethanol. An unusual reaction occurs in which part of  ${\rm Fe}^{3^{\dagger}}$  is reduced to  ${\rm Fe}^{2^{\dagger}}$  and a crystalline solid deposits. This has been shown to be an intervalence species of the type  $[{\rm Fe}^{{\rm III}}({\rm Fe}^{{\rm II}}({\rm aao})_3)_2]$ -  ${\rm Fe}^{{\rm III}}{\rm Cl}_4$  (1:1 electrolyte in nitromethane and nitrobenzene solutions). In this both iron(III) atoms are high-spin (five unpaired electrons) while iron(II) is low-spin. The iron(III) atom in the cation is believed to be bound in an octahedral fashion to the six oximato oxygen atoms of two  ${\rm cis}{\rm -Fe}({\rm aao})_3^-$  moieties. This is shown

schematically in XXII in which the oxygen atoms coming from the same  $Fe(aao)_3$  unit carry the same number on the top. The Fe-O

$$0^{2} - 0^{2}$$

$$0^{1} - 0^{2}$$

$$0^{1} - 0^{2}$$

(XXII)

for the FeO<sub>6</sub> coordination sphere is observed at  $^{\circ}$  430 cm<sup>-1</sup>. The  $^{\circ}$  band of FeCl<sub>4</sub> anion is present at  $^{\circ}$  380 cm<sup>-1</sup>. The corresponding perchlorate [Fe<sup>III</sup>(Fe<sup>II</sup>(aao)<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> results from a direct reaction between iron(II) perchlorate and Haao. In the infrared Fe-O stretch is again seen at  $^{\circ}$  430 cm<sup>-1</sup> (the presence of a shoulder at  $^{\circ}$  400 cm<sup>-1</sup> suggests distortion from an octahedral geometry). Infrared data supports the presence of a completely ionic tetrahedral ClO<sub>4</sub>. The species [Fe<sup>III</sup>(Fe<sup>II</sup>(aao)<sub>3</sub>)<sub>2</sub>]Br is also briefly reported. The [Fe(Fe(aao)<sub>3</sub>)<sub>2</sub>]X (X = ClO<sub>4</sub>, Br) shows a g'  $^{\circ}$  4.3 epr line characteristic of rhombic FeO<sub>6</sub> sphere. When X = FeCl<sub>4</sub>, an intense additional band at g  $^{\circ}$  2.0 (due to FeCl<sub>4</sub>) is also observed.

The chemical interconversion of the various species viz.,  $NaFe(aao)_3.H_2O$ ,  $HFe(aao)_3$ ,  $[Fe(Fe(aao)_3)_2]FeCl_4$  and  $Fe(Fe(aao)_3)_2$ .  $ClO_4$  are described. For example  $[Fe(Fe(aao)_3)_2]FeCl_4$  reacts with sodium hydroxide to yield two moles of  $NaFe(aao)_3.H_2C$  and two moles of Iron(III) hydroxide. On the other hand  $NaFe(aao)_3.H_2O$  reacts with one mole of Iron(III) to regenerate  $[Fe(Fe(aao)_3)_2]FeCl_4$ . Since

[Fe(Fe(aao)<sub>3</sub>)<sub>2</sub>]X (X=FeCl<sub>4</sub> or ClO<sub>4</sub>) contain both iron(II) and iron(III) linked by a bridge system one may expect a low-energy intervalence charge transfer transition: Fe(II)  $\rightarrow$  Fe(III) (class II mixed valence system). However in practice we have not been able to locate such an intervalence bond. It is believed that this band lies under the very intense  $\sim$  600 nm iron(II)  $\rightarrow$  ligand transition making a direct observation impossible.

A species of the type  $\operatorname{Ni}\left(\operatorname{Fe}\left(\operatorname{aao}\right)_{3}\right)_{2}$  is briefly reported. This is believed to have a structure similar to that of  $\left[\operatorname{Fe}\left(\operatorname{Fe}\left(\operatorname{aao}\right)_{3}\right)_{2}\right]^{\top}$  with  $\operatorname{Fe}^{3^{+}}$  replaced by  $\operatorname{Ni}^{2^{+}}$ . The  $\operatorname{Fe}\left(\operatorname{aao}\right)_{3}^{-}$  thus acts as versatile donor by virtue of oximato oxygens. It binds  $\operatorname{H}^{+}$ ,  $\operatorname{Na}^{+}$ ,  $\operatorname{Ni}^{2^{+}}$  and  $\operatorname{Fe}^{3^{+}}$  and a variety of other metal ions which are not considered in this thesis.

### VITAE

Born on January 14, 1949 at Chickmagalur (Karnataka), the author obtained his B.Sc. (Hons.) and M.Sc. degrees from Bangalore University in 1969 and 1971 respectively. He joined the Ph.D. programme of the Department of Chemistry, Indian Institute of Technology, Kanpur in 1972. He is presently continuing in the same Institute as a Research Assistant.